This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

3 3433 06639745 0

SIDEROLOGY: THE SCIENCE OF IRON

SIDEROLOGY

THE SCIENCE OF IRON

BY

HANNS FREIHERR V. JÜPTNER

LECTURER AT THE SCHOOL OF MINING AT LEOBEN

TRANSLATED FROM THE GERMAN

BY

CHARLES SALTER

THE CONSTITUTION OF IRON ALLOYS AND SLAGS

WITH ELEVEN PLATES AND TEN ILLUSTRATIONS

LONDON

SCOTT, GREENWOOD & CO.

19 LUDGATE HILL, E.C.

1902

[*The sole Right of Translation into English rests with the above Firm*]

THE NEW YORK
PUBLIC LIBRARY
255391
ASTOR, LENOX AND
TILDEN FOUNDATIONS

PREFACE

THE first inception of the present work originated in the author's lectures on the "Theories of Hardening," delivered at the Royal Mining Academy of Mining at Leoben, 1898–99. A conviction arose in his mind that a compilation of the present state of our knowledge with regard to iron would be the more desirable, both for students and practical metallurgists, owing to the existing lack of such a work, the literature on the subject being scattered throughout a variety of technical journals, and therefore difficult of access; whilst at the same time the study of the original works is aggravated by their being partly based on the most recent acquirements of highly divergent branches of science, and partly by their having been written by various authors at very different times, thus entailing considerable trouble in collating the whole in a uniform manner.

Another object of the work is to lay before the investigator in this field a succinct account of the researches already performed, and to display to the consumer of iron and steel the connection between the various properties, the constitution, and the methods of working the materials in question.

Now, these divergent objects necessitate a more comprehensive treatment of the subject than would suffice for each of them separately. For example, in the case of lectures to constructors of machinery, the chemical constitution of the

materials might be treated more briefly, whereas this point must necessarily be more fully dilated upon for metallurgists.

For all readers practically engaged in the subject of the work, it appeared to the author indispensably necessary to give a description of the modern theory of solution, on which indeed our present hypotheses are founded.

The work itself falls into three portions, the first of which, after describing the theory of solution, deals with the microscopical and chemical constitution of iron (with its supplementary constituents) and slags. The second part will treat of the connection between the chemical composition, the working, the microscopical structure, and the other properties of iron and steel; whilst the third part will deal with the reaction between the metal, slags, and other re-agents.

A brief outline having been given of the ground plan of the work, a few words may be devoted to the title selected. Like every child, each book must have a name. Titles like "Theoretical Metallurgy of Iron," "Chemistry of Iron," etc., would be insufficient to denote the contents; and even "Siderography" (based on Osmond's *Metallography*) is not precise enough. Probably the title chosen, *Siderology*, will best express the subject of the book, namely "The Science of Iron."

That the work itself may prove useful to many, help to spread the science of iron throughout wider circles, and may find friends and collaborators not only among scientists but also among the producers and consumers of iron, is the sincere wish of

THE AUTHOR.

DONAWITZ, *August* 1900.

CONTENTS

PAGE

INTRODUCTION 1

THE CONSTITUTION OF IRON ALLOYS AND SLAGS

BOOK I

THE THEORY OF SOLUTION

CHAP.

I. Solutions 7
II. Molten Alloys: Varieties of Solutions 14
III. Osmotic Pressure 19
IV. Relation between Osmotic Pressure and other Properties of Solutions 25
V. Osmotic Pressure and Molecular Weight of the Dissolved Substance 38
VI. Solution of Gases 45
VII. Solid Solutions 48
VIII. Solubility 55
IX. Diffusion 65
X. Electrical Conductivity: Constitution of Electrolytes and Metals 70
XI. Thermal Expansion 76

BOOK II

MICROGRAPHY

I. General 81
II. Microstructure 95
III. The Micrographic Constituents of Iron 100
IV. Relation between Micrographical Composition, Carbon Content, and Thermal Treatment of Iron Alloys . . 123
V. The Microstructure of Slags 137

BOOK III

CHEMICAL COMPOSITION OF THE ALLOYS OF IRON

CHAP.		PAGE
I.	Introduction	144
II.	Constituents of Iron Alloys: Carbon	148
III.	Constituents of the Iron Alloys: Carbon—Opinions and Researches on Combined Carbon	175
IV.	Opinions and Researches on Combined Carbon (*Continuation*)	190
V.	Opinions and Researches on Combined Carbon (*Conclusion*)	213
VI.	Applying the Curves of Solution Deduced from the Curves of Recalescence to the Determination of the Chemical Composition of the Carbon present in Iron Alloys	223
VII.	The Constituents of Iron: Iron	237
VIII.	The Constituents of Iron Alloys: Manganese	245
IX.	Remaining Constituents of Iron Alloys—	
	A. Silicon	254
	B. Phosphorus	256
	C. Sulphur	270
	D. Chromium	271
	E. Tungsten	272
	F. Molybdenum	272
	G. Nickel, Copper, Titanium	272
	H. Oxygen	273
X.	Gases	274

BOOK IV

THE CHEMICAL COMPOSITION OF SLAG

I.	Introductory	289
II.	Silicate Slags	291
III.	Calculating the Composition of Silicate Slags	303
IV.	Phosphate Slags	317
V.	Oxide Slags	329
	APPENDIX TO PAGES 226 and 233	333
	INDEX	335

SIDEROLOGY: THE SCIENCE OF IRON

INTRODUCTION

THE science now termed siderology comprises the study of iron and its alloys, and is a subject only as yet in its infancy.

True, the beginnings are to be found in the literature and text-books on iron smelting a long way back, but it is only within the last few years that the construction of this science has been undertaken, and that, too, with considerable eagerness. At present a large number of scientists are engaged in this direction, driving shafts and headings, as it were, into the unexplored regions of this science, so that even now it is evident that the subject will be thoroughly opened up within a reasonable time.

As in the case of other sciences in their process of establishment, so also here: many experimental attempts have had to be abandoned because they led only to barren results, sometimes even collapsing altogether when not sufficiently shored up. And just as in ancient mines the work was not very productive, because hammer and chisel were the only tools, and their effects had to be eked out by the aid of fire, whereas nowadays much more successful results are obtained by means of drilling-machines and blasting; so is it with siderology: since the introduction into this science of

such powerful supplementary tools as the microscope and physical chemistry, the winning proceeds at a rapid rate.

It was, in fact, the microscopy of metals that gave the first impulse to the foundation of our science. It was found that the metallic alloys in general are far from homogeneous, but consist, as a rule, of elements of various structure, and attention was directed to ascertaining the chemical composition of these latter. In this way metallography (Osmond) arose, and that portion of this science which deals with the alloys of iron has received the name of siderography (Jüptner).

Now the names metallography and siderography are analogous in construction to petrography or the science of rocks, and refer only to the sciences dealing with the investigation and description of the morphological and more intimate chemical composition of the metals (that is to say, of iron) or rocks. As regards the substances lying in the domain of these sciences, their concern with these substances is confined to the condition in which the latter actually come for examination, and they disregard the circumstances under which the substances have been formed, or the modifications which they undergo under certain conditions.

If now these other circumstances be taken under consideration, we arrive at a new science, standing towards the foregoing in about the same relation as geology is towards petrography; and this science of iron and its alloys is consequently entitled siderology (Jüptner).

Consequently siderology is the science which not only ascertains the more intimate morphological and chemical compositions of the iron alloys (siderography), but also examines the modifications produced in this composition by external influences (mechanical and thermal treatment, etc.), and the relation existing between this composition and the physical and mechanical properties of these alloys.

This explanation, however, does not sufficiently define the

limits of siderology. This science occupies itself, namely, not merely with the modifications of composition and properties sustained by the iron alloys under mechanical treatment by rapid or protracted heating or cooling, etc., but also concerns itself with the alterations produced in the metal by reaction with other substances, and therefore attributable to oxidising, carbonising, and similar chemical processes, or to phenomena of solution.

The similarity between petrography and siderography on the one hand, and geology and siderology on the other, has already been mentioned; but there is still another prominent analogy existing with regard to the means employed by both groups of allied sciences. The two first being descriptive sciences, chiefly rest upon two bases, morphology and chemistry, and therefore mainly employ two adjuncts—the microscope and chemical analysis. On the other hand, the last two sciences are based not merely on the first, but also on a whole series of other supplementary sciences. Now this circumstance necessitates a brief treatment of the most important parts of these supplementary sciences at the commencement of the present work. We will therefore first deal with the properties of solutions and the most essential parts of the theory of solution; then will follow the morphological and chemical composition of the iron alloys and slags, as well as a description of their chemical and mechanical properties; and then only shall we arrive at siderology in the more restricted sense of the term.

;IENCE OF IRON

SIDEROLOGY: THE SCIENCE OF IRON

solid form occurs at a certain temperature, which also depends on the degree of concentration, leaving the now more dilute mother liquor in a liquid form, the latter subsequently solidifying throughout the entire mass on being cooled further.

If these temperatures of the separation of ice or salt, and also the solidification temperature of the residual mother liquor be represented in graphical form, the curve plotted in Fig. 1 of Plate I. will be obtained. In these figures the curve A B represents the separation of ice, the curve B C the separation of solid salt; and the line D B E the solidification of the residual mother liquor.

To make the matter clearer, we will trace the behaviour of several common-salt solutions of various strengths, in the course of cooling.

With a 10 per cent. solution the separation of pure ice, free from salt, occurs at -8° C.; the fluid residual mother liquor contains 23·5 per cent. of sodium chloride, and sets in its entirety at -22° C.

From a solution containing 25 per cent. of sodium chloride the solid salt is deposited at -12° C., whilst the still fluid mother liquor, which also contains 23·5 per cent. of NaCl, solidifies at -22° C. as before.

Finally, a solution of 23·5 per cent. of sodium chloride solidifies suddenly and entirely, without any previous separation of ice or salt, also at -22° C.

A closer examination of these conditions, however, leads to further observations.

The melting point of pure ice, or the freezing point of pure water, is 0° C. If the water contains common salt in solution, the separation of ice, *i.e.* the freezing of the excess water, occurs at a temperature the further below 0° C. in proportion as the amount of salt is greater. We may therefore also regard the curve A B in Fig. 1 as the melting point

curve of water in the presence of common salt, and hence arrive at the conclusion that the solidification point of the solvent is lowered by the presence of a dissolved substance. With the exception of a special class of solutions, which we shall have to mention later, this is a rule of general application.

On the other hand, we find that the temperature at which the separation of solid salt occurs in concentrated solutions increases with the saline content, and approaches nearer and nearer—though this is not visible in Fig. 1—the melting point of the salt, which point is attained when the solution contains 0 per cent. of the water and 100 per cent. of common salt.

It is seen that concentrated and dilute solutions behave alike; during cooling the excess of solvents separates out in the solid form, the temperature of separation lying, in most cases, the further below the melting point of that constituent, the larger the proportion of the second constituent present. Does not this behaviour naturally lead to the assumption that dilute solutions represent merely a reverse condition to the case of concentrated solutions, and that, for example, a dilute aqueous solution of common salt is to be regarded as a concentrated solution of water in common salt?

Certainly at first this assumption appears somewhat remarkable; but we shall very soon see that it is correct. A further conclusion, however, is that distinction between solvents and dissolved substances must be abandoned, and that we can only speak of a mutual solution on the part of two or more substances.

If we again examine what goes on in the cooling of an aqueous solution of common salt, it is remarkable that in all cases, independently of the percentage composition of the solution, the final residual fluid mother liquor has the same composition, and solidifies at the same temperature.

Now, as constant composition and constant melting point were formerly regarded as characteristic of chemical compounds, these residual mother liquors were also regarded as such, and received the name of cryohydrates (by Gouthrie), because aqueous solutions were mostly in question, and because these compounds seemed to be formed in the cold.

However, it was only in the rarest cases that these cryohydrates appeared to have a constitution in accordance with stöchiometric conditions, on which account doubt was soon raised as to whether they really were actually chemical compounds, and, as a matter of fact, strict proof was soon afforded that the cryohydrates are merely a mechanical, a (mostly foliated) juxtaposition of the constituents of the solution. Consequently the name also was changed by Gouthrie to "Eutectic" in 1884. An advisable distinction is drawn between *eutectic solutions*, in which the two constituents are present in a state of solution, and *eutectic mixtures*, wherein the constituents are separated by an interval of space.

Nevertheless the phenomena occurring during the cooling of solutions are not in all cases so simple as with aqueous solutions of common salt, inasmuch as separation may occur not merely of one constituent of the solution, but sometimes even of a combination of the two constituents of the solution.

Thus, in the case of a solution of Glauber salt saturated at 33° C., a separation of the anhydrous salt (Na_2SO_4) occurs at this temperature, whereas at a lower temperature the compound $Na_2SO_4 + 10H_2O$ crystallises out.

A solution of manganese sulphate gives—

At 100° C., crystals of $MnSO_4 + 3H_2O$; between this and 20° C., crystals of $MnSO_4 + 6H_2O$; below 6° C., crystals of $MnSO_4 + 7H_2O$.

Special interest attaches to the researches of Roozeboom[1] on the hydrates of ferric chloride, which we will therefore proceed to describe in detail.

Fig. 2 of Plate I. gives the precipitation curves of aqueous solutions of ferric chloride, in a similar manner as Fig. 1 does for aqueous solutions of common salt, except that the amount of ferric chloride present in the solution is not expressed in percentages, but in molecules of Fe_2Cl_6 per 100 mol. of water. The curve A B corresponds to the separation of ice from the "dilute" solution; K L corresponds to the separation of anhydrous ferric chloride from the concentrated solution; whilst the other curves represent the separation of hydrates containing a larger quantity of water in proportion as the amount of the salt decreases.

Therefore, in accordance with the degree of concentration, there are separated from the aqueous solution of ferric chloride six different compounds, as follows, in regular order:—

Fe_2Cl_6; $Fe_2Cl_6 + 4H_2O$; $Fe_2Cl_6 + 5H_2O$; $Fe_2Cl_6 + 7H_2O$; $Fe_2Cl_6 + 12H_2O$; and H_2O.

This case follows the general rule (except with the compound $Fe_2Cl_6 + 7H_2O$) that the composition of the separated compounds is the more complex, and their molecular weight therefore heavier, the lower the separation temperature.

The portions of the curve marked D N, D O, F M, F P, H R correspond to labile conditions; at the point of intersection B, equilibrium exists between ice and the hydrate containing the largest proportion of water; at D F H, between the adjacent hydrates; and, finally, at K, between the hydrate poorest in water and the anhydrous salt. In all these cases the composition of the solution is intermediate between that of the two solid bodies, since the one branch of the curve of solution collides with the neighbouring branch of the next lowest hydrate. The points indicated are at $-55°$, $27°{\cdot}4$, $30°$,

[1] *Zeits. für phys. Chemie*, x. p. 477.

55°, 66°, which are also the temperatures at which the solutions solidify to eutectic mixtures of the two hydrates.

In order to gain a proper idea of the prevailing conditions, let it be imagined the concentration and temperature of a ferric chloride solution be represented by a point situated above the part bounded by the portion of the curve A B C D E F G H I K L; in cooling, the solution will then first traverse a vertical line of constant composition, and will intersect one portion of the curve, say F G H, on reaching a given temperature. Supersaturation being precluded, there immediately ensues separation of the solid substance corresponding to this portion of the curve, *e.g.* $Fe_2Cl_6 + 5H_2O$. As cooling proceeds further the liquid portion of the solution will traverse the curve towards lower temperatures, until it reaches the end point at which a second solid body is separated, and complete solidification occurs. If the solution correspond exactly to the composition of a hydrate, it will become entirely solid at the melting point of this latter; or if the composition correspond to the intersection of the curves of two adjacent hydrates, the solidification will take place at the temperature corresponding thereto.

A remarkable peculiarity will be noticed in the evaporation of ferric chloride solutions, more particularly between 30° and 32° C., namely, that a dilute solution will, in course of evaporation, first dry to $Fe_2Cl_6 + 12H_2O$, then re-liquefy, afterwards dry again to $Fe_2Cl_6 + 7H_2O$, then liquefy once again, to dry a third time as $Fe_2Cl_6 + 5H_2O$, the entire series of these phenomena corresponding to stable conditions.

As follows from the branch curves B C D, D E F, etc., there are, between certain intervals of temperature, two saturated solutions of different composition, in equilibrium with the solid hydrate, the one containing always more, the other less, water than the solid hydrate. Both are, however, thoroughly stable, and in no way supersaturated, this latter condition

first occurring in a solution belonging to a point situated below the portion of the curve A B C D E F G H I K L; and by the introduction of a fragment of the corresponding solid hydrate the supersaturation is removed, whereby, according to circumstances, the content of ferric chloride is diminished or increased, according as a saturated solution of the first or second category is formed.

CHAPTER II

MOLTEN ALLOYS: VARIETIES OF SOLUTIONS

THE idea of regarding molten alloys as solutions is one that readily suggests itself, and, as a matter of fact, the two behave in a very similar manner in cooling. Thus, if we take the silver-copper alloys as an example, these bodies give the separation curves shown in Fig. 3 of Plate I., the similarity between which and those of the aqueous solutions of common salt is unmistakable. In these—

a is the fusing point of pure silver (960° C.);

a b is the separation point of pure silver from alloys rich in silver;

b c is the separation temperature of pure copper from alloys rich in copper;

c is the fusing point of pure copper (1090° C.);

d b e is the solidification of the eutectic alloy of silver and copper (Ag. 72 per cent., Cu. 28 per cent.) at 775° C.

The method of determining the curves of solubility and fusing point of an alloy can be gathered from the following simple observation:—

If a substance be heated to any convenient high temperature and then allowed to cool slowly, the rate of cooling is the more rapid at first, but continually diminishes as the temperature falls and time goes on. The progress of the cooling can be represented in a graphical manner by selecting the temperature and time as co-ordinates, and in this way curves of cooling are obtained. If the substance under in-

vestigation does not undergo any change of condition, accompanied by an evolution or absorption of heat during the cooling process, then the curve of cooling will be continuous, and of the type represented in Fig. 4 of Plate I. (*a b*).

If, however, a physical or chemical change, accompanied by the evolution of heat, is sustained by the body during cooling, then the curve will exhibit interruptions, which—according to the dimensions and rapidity of the liberation of heat in question—will appear, either as a sudden rise (Fig. 5, Plate I.) or as a prolonged constancy (Fig. 6, Plate I.) of temperature, or finally, as merely a local retardation of the decrease of temperature (Fig. 7, Plate I.).

The points at which these interruptions occur are known as "critical points," and the corresponding temperatures are termed "critical temperatures," or, when the interruption extends over a large interval of temperature, "critical temperature zones."

Now all bodies at all capable of existing in a liquid and a solid state of aggregation, possess a certain latent heat of fusion, *i.e.* they remain solid when heated just to fusing point, and, when heated further, gradually liquefy, the temperature, however, remaining constant until complete liquefaction has ensued, and only continuing to rise when the application of heat is maintained thereafter.

If now, on the other hand, a body be heated above its fusing point—take silver, for example—and then slowly cooled, the temperature will fall in a regular manner until the solidification point is reached (in this case 960° C.). At this point, however, it remains constant until the entire mass of the silver has become solid, and only then does it resume its downward course.

When, instead of a homogeneous body, we have to deal, for example, with an alloy of silver and copper, then the metal which is in excess solidifies first, and therefore gives a

critical point, whereas the remainder of the mass still rem liquid. Cooling therefore continues until the rest—in case a mixture of the two metals, a *eutectic alloy*—solid suddenly and all at once, thus furnishing the second cri point.

The critical points of a series of alloys of the same m having been determined in this manner, all that is neces to obtain the corresponding curves of solution is to arra these points in a network of co-ordinates in accordance the chemical composition of the alloys.

Numerous researches of this kind have demonstrated these curves of solution exhibit divergent characteristic form, according to the mutual behaviour of the compon of the solution; and for this reason solutions have classified into a number of groups, as follows:—

1. *Solutions the compounds of which do not form chemical compounds or isomorphous mixtures with each othe*

The solution curves of this group have the typical represented in Fig. 8 (Plate I.), *a* being the fusing poin the constituent B; *c*, that of the constituent A; *a b*, c sponding to the separation of B; *b c*, to that of A in the form; and finally, *d e*, the solidification of the eutectic mix Such solutions therefore exhibit three different solution cu which mutually intersect at a point corresponding to composition of the eutectic solution.

2. *Solutions the constituents of which form together isomorphous mixture, but not a chemical compound.*

As can be seen from Fig. 9 (Plate I.), solutions of class exhibit only a single curve of solution, invariably necting the fusing points of the two components. Here the fusing point of B, *b* that of A, and *a b* represents sudden and simultaneous solidification of both constitu of the solution.

This peculiar behaviour may be readily explained by

THE NEW YORK
PUBLIC LIBRARY
ASTOR, LENOX AND
TILDEN FOUNDATIONS
L

assumption that each member of a series of such solutions is eutectic; each such eutectic solution has therefore a different composition, and also a different fusing point.

The two foregoing groups form the main types, by the combination of which a series of sub-types can be obtained. Such are the following:—

3. *Solutions the components of which form chemical combinations, but do not form, either together or with these combinations, any isomorphous mixture.*

A representation of these conditions is given in Fig. 10 of Plate I. Here *a* is the fusing point of the component B, *e* that of A; *c*, however, being the fusing point of the compound $A_x B_y$. *a b* corresponds to the separation of B, *b c* and *c d* that of the compound $A_x B_y$, and *d e* that of A, in the solid state. Finally, *f g*, *h i* correspond to the solidification of the eutectic solution of B and $A_x B_y$, or A and $A_x B_y$.

As the figure shows, this curve corresponds to the arrangement of two curves of the first type.

4. *Solutions the components of which form chemical compounds furnishing an isomorphous mixture with one of the components* (Fig. 11, Plate I.).

Here *a*, *d*, and *c* are the fusing points of the components B, A, and the compound $A_x B_y$; *a b* represents the solidification of the excess of B; *b c* that of the compound $A_x B_y$; *c d* that of the isomorphous mixture of A and $A_x B_y$; and finally, *e f* the solidification of the eutectic mixture of B and $A_x B_y$. The curve is therefore a combination of the types 1 and 2.

5. *Solutions the components of which form no chemical compounds together, but furnish isomorphous mixtures within certain percentage limits.*

Two instances of this type are illustrated by Figs. 12 and 13 (Plate I.). In Fig. 12, *a* and *c* represent the fusing points of the two constituents. The excess of B solidifies at *a b*, a eutectic mixture of constant composition solidifies at *d b*, and

the isomorphous mixture—*i.e.* a eutectic mixture of variable composition—solidifies at *b c*. In Fig. 13, *a* and *d* are the fusing points of the components; the excess of B and A separates at *a b* and *c d* respectively, in the solid state; the solidification of two different, but constant, eutectic solutions occurs at *e b* and *f g*, and the isomorphous mixture solidifies at *b c*.

In many instances practical conclusions of industrial value have been drawn from the fusing-point curves, theory afterwards affording an explanation of the phenomena already known and utilised. As an instance of this may be cited the important operation of desilvering lead with zinc, a process that would, however, take too long to fully describe here.[1]

[1] Bodländer, *Berg- u. Hüttenm. Ztg.*, 1897, p. 331.

CHAPTER III

OSMOTIC PRESSURE

When a concentrated aqueous solution is covered with a layer of water, as it may be by the exercise of a little care, the two liquids will be superposed and separated by a reflecting surface. If, however, the whole be left to itself for a while, the conditions will be found to have sustained alteration, the dissolved substance commencing to raise itself against the influence of gravitation and to distribute in the supernatant water; and this movement does not cease until the substance has become uniformly distributed throughout the entire amount of water.

This phenomenon can be readily observed by employing a strongly coloured solution for the experiment. At the outset the water immediately above the plane of separation of the two liquids begins to be coloured; the coloration then extends further and further upwards, at the same time becoming progressively deeper near the plane of separation, which latter also recedes to a lower level.

The experiment may be somewhat modified by arranging a so-called semi-permeable wall—which allows the passage of water, but not of the dissolved substance—between the two liquids. A wall of this kind may be obtained, for example, by impregnating a porous earthenware cell with a solution of copper sulphate, then carefully rinsing it and filling it with a solution of potassium ferrocyanide. In

this manner a coherent precipitate of copper ferrocyanide is deposited on and in the pores of the earthenware, which deposit has the property of permitting the transpiration of water, but not of any sugar (for example) that is dissolved therein. A similar effect is produced by a number of other amorphous deposits, such as ferric oxide, gelatin tannate, silica, etc.

If a solution of sugar be placed in a cell prepared in the above manner, the latter then closed with a cork and immersed in a vessel of water, the pressure obtaining in the cell can be determined by the aid of a manometer passed through the cork, and this pressure will be found to attain a certain maximum height, which depends on the concentration of the sugar solution, and on the temperature.

These phenomena can be rendered visible in the following manner:—The cylindrical vessel, *a b c d* (Fig. 14, Plate I.), contains a solution of sugar, over which is placed a movable plunger, *e f*, which is made of semi-porous material, and attached to a stem, *g h*, the plunger being surmounted by pure water. The sugar, which endeavours to expand, but is prevented by the plunger *e f*, exerts pressure on the under surface of the latter, and moves it, so that water traverses it from above, and enters the sugar solution, which is thereby diluted. If now the stem of the plunger be subjected to a downward pressure equal to the upward pressure exerted by the sugar, the plunger will retain its position unaltered, and the concentration of the sugar solution will remain unchanged; on the other hand, if the pressure on the plunger stem exceed the upward pressure, the plunger will descend, water will transfuse from below, and the strength of the sugar solution will increase.

This pressure, exerted by a dissolved substance in its solution, is termed its "osmotic pressure."

Pfeffer, who made a thorough study of these conditions, found (in 1877) that—

1. The osmotic pressure of a solution is proportional to its concentration. Thus, for sugar solutions he found—

Concentration.	Pressure.	Ratio.
1 per cent.	53·5 cm.	53·5
2 „	101·6 „	50·8
2·74 „	151·8 „	55·4
4 „	208·2 „	52·1
6 „	307·5 „	51·3

2. That in the case of all dissolved substances the osmotic pressure increases in proportion to the temperature, *e.g.*:

	Pressure.	At	At	Observed.	Calculated.
Saccharose . . .	54·4	32°	14°·15	51·0	51·2
„ . . .	56·7	36°	15°·5	52·1	52·9
Sodium tartrate . .	156·4	36°·6	13°·3	143·2	144·3
„ „ . .	98·3	73°	13°·3	90·8	90·7

(This calculation is based on the supposition that the coefficient 0·00367, applicable to the case of gases, is also correct here.)

These two laws, which have been demonstrated accurate by numerous experiments, prove that osmotic pressure follows Boyle's law as well as that of Gay-Lussac, and can therefore be expressed by the well-known equation for gases—

$$p\,v = \mathrm{R}\,.\,\mathrm{T},$$

so that there remains for determination only the value of the constant R, which, as is well known, is uniform for molecular mixtures of different gases.

If we take the molecular weight (in grams) as the unit, we have, for example, in the case of oxygen—

Pressure of one atmosphere: $p = 1033$ grms.;

Volume of the gram-molecule of oxygen (32 grms.) at 0° C. and 760 mm. pressure: $v = 22{,}380$ c.c.;

Absolute temperature: $T = 273$;
and therefore—

$$R = \frac{p \cdot v}{T} = 84700.$$

In the case of a 1 per cent. solution of sugar, Pfeffer determined the osmotic pressure at 0° C. as 49·3 cm. of mercury, *i.e.* $49{\cdot}3 \times 13{\cdot}59 = 671$ grms. per sq. cm. If, in the equation

$$p\,v = R\,T,$$

we substitute the experimentally determined value (for gases) $R = 84700$, then we obtain for the 1 per cent. sugar solution—

$$v = \frac{R \cdot T}{p} = \frac{84700 \times 273}{671} = 34460 \text{ c.c.}$$

Consequently a 100 per cent. solution of sugar would occupy only the one-hundredth part of this space, *i.e.* 344·6 c.c., a figure corresponding with the molecular weight of sugar ($C_{12}H_{22}O_{11} = 342$).

Therefore the osmotic pressure of a dissolved substance is the same as the pressure that would be exerted by the same substance if it were occupying in the gaseous state the same space as occupied by the solution, and at the same temperature.

Hence, as J. H. van't Hoff has shown, the gas equation $p\,v = R\,T$ is equally applicable to solutions.

Moreover, it has been shown that Avogadro's law: that at equal temperature and equal pressure equal volumes of different bodies contain an equal number of molecules, applies both to bodies in the gaseous form and also in a state of solution.

A perfect analogy, therefore, exists between gases and solutions, and we may consequently lay down for the latter the following general definition:—

Solutions are molecular mixtures of several substances, the constituents of which mixtures exhibit the peculiarity of following the laws relating to gases.

This definition, however, is not only applicable to all gaseous and fluid mixtures, but also, as numerous experiments have demonstrated, to several solid mixtures, and consequently there must be both solid, liquid, and gaseous solutions.

Now it is well known that the laws of Boyle, Avogadro, and Gay-Lussac apply in merely an approximate manner to gases, inasmuch as the latter exhibit deviations from these laws, and the more so in proportion as the liquefaction temperature of the gases is approached. This is due to the circumstance that, in considering changes of volume on the part of gases, only the intramolecular spaces between the molecules of gas, and not the entire volume occupied, have to be borne in mind on the one hand, whilst on the other a certain mutual action—attraction—goes on between the individual molecules, even in the case of gases; this action is the cause of cohesion in liquid and solid bodies, in which cases it is apparent in a much higher degree.

Now, whereas the combined laws of Boyle and Gay-Lussac can be expressed by the equation $p \cdot v = \mathrm{R\,T}$ (R being equal to $\frac{p_0 v_0}{273}$), Van der Waal (1879), bearing in mind the above-mentioned circumstance, laid down the equation—

$$\left(p \times \frac{a}{v^2}\right)(v - b) = \mathrm{R\,T}$$

to express the relation between the pressure, volume, and temperature of gases, and it has been proved that this equation applies to permanent gases as well as to vapours and liquids.

Hence, at the first glance, it must appear surprising that osmotic pressure should follow, not the Van der Waal law, but the Boyle-Gay-Lussac law. Nevertheless it will be evident, on closer consideration, that the case could not be otherwise. The methods hitherto employed for determining

the osmotic pressure invariably give the osmotic energy P, *i.e.* the energy required to effect the removal of unit volume of the pure solvent from solution, and this value, when multiplied by the unit volume, has proved equal to the gas pressure. If, however, we assume that the pressure of the dissolved substance is increased in the proportion $1 : (1 - b)$, in consequence of the correction of volume, b expressing the fractional part of unit volume by which the space available for the movement of the molecule is diminished, it will then amount to $\frac{P}{1-b}$; the osmotic energy to be developed during the removal of unit volume of solvent then being—

$$\text{Pressure} \times \text{volume} = \frac{P}{1-b}(1-b) = P,$$

since the volume over which the pressure has to be resisted is for the same reason diminished in the proportion $(1 - b) : 1$. Consequently the correction for volume is entirely dispensed with in these methods of determination.

We shall see later on that osmotic pressure follows the Boyle-Mariotte law, even in the case of high concentrations.

CHAPTER IV

RELATION BETWEEN OSMOTIC PRESSURE AND OTHER PROPERTIES OF SOLUTIONS

As a general rule, the properties of any body are modified by the presence of a second body in solution therein. The properties of special interest to us in this connection are: the vapour tension, boiling point, and solidification point of the solvent.

To take the vapour tension first, a distinction must be drawn between cases wherein only one constituent of the solution is volatile, and where both constituents vaporise together.

In the latter, and more general eventuality, the vapour tension of the liquid mixture is equal to the sum of the partial tensions of the individual constituents, whereas in the former case the vapour tension is identical with the partial tension of the solvent.

Since the first and special case is the one of greatest interest for us, we will more closely consider this one first.

1. Let us imagine the case of a solution containing only a single volatile constituent, as being contained in the vessel L (Fig. 15, Plate I.). Let this vessel be closed at A A by a semi-permeable wall, which only allows the volatile constituent of the solution (*e.g.* water) to pass through; and be also fitted with an ascending tube, H. Moreover, let this vessel be immersed, as regards its lower portion, in the pure volatile solvent (in this case water), the whole being closed in

an air-tight manner, and maintained at a temperature, T. Under these conditions water will continue to force its way through A A towards L, and raise the height of the column of liquid in the ascending tube until equilibrium is established, *i.e.* until the vapour tension p of the water is equal to the vapour tension of the solution p_1, increased by the pressure of a column of vapour of the height H, acting on W. If this were not the case, then either an evaporation of water must occur in W, to be condensed in H and return to W through L and A, or *vice versâ*, which implies that any amount of external work could be done at the mere cost of the heat present in the environment, a circumstance contrary to the second principal axiom of the mechanical theory of heat.

To calculate the pressure of this column of vapour we revert to the expression of the Boyle-Gay-Lussac law—

$$p\,v = \frac{p_0\,v_0}{273}\,.\,\mathrm{T} = \mathrm{R\,T}$$

and refer this expression to a gram-molecule of the gas (*i.e.* the molecular weight of the gas in grams), whence, according to Regnault's measurements of the density of the permanent gases, that one gram-molecule of this gas, enclosed at a temperature of 0° C. in the space of one litre, exerts a pressure $p_0 = 22{\cdot}35$ atmospheres. Hence we obtain—

$$p\,v = \frac{22{\cdot}35}{273}\,.\,\mathrm{T} = 0{\cdot}0819\,\mathrm{T};\ \text{therefore}\ v = \frac{0{\cdot}0819\,\mathrm{T}}{p}$$

whence results, for the specific gravity of the vapour at the temperature T, the volume v, and the pressure p, referred to water as unity, *i.e.* the weight of a cubic centimetre of the vapour in grams—

$$\frac{\mathrm{M}}{1000\,v} = \frac{\mathrm{M}\,.\,p}{0{\cdot}0819\,\mathrm{T}\,.\,1000} = \frac{\mathrm{M}\,.\,p}{81{\cdot}9\,\mathrm{T}}\,.$$

If, as will be assumed for the sake of simplicity, we have to do with dilute solutions, we may state $p = p_1$, and ignore the variation in the density of the vapour at different altitudes.

Moreover, if we remember that 1 atmosphere is equal to the pressure of 760 mm. of mercury, and term the specific gravity of mercury σ, we then have for the hydrostatic pressure of the column of vapour of the height H—

$$p - p_1 = \frac{\mathrm{H\,M}\,.\,p'}{0{\cdot}0819\ \mathrm{T}\,.\,1000\,.\,76\,.\,\sigma}\ \text{atmos.}$$

If, furthermore, we express the specific gravity of the solution—which in case of dilute solutions will differ but little from the specific gravity of the solvent—by S, then we obtain the osmotic pressure of the solution—

$$\mathrm{P} = \frac{\mathrm{H}\,.\,\mathrm{S}}{76\,.\,\sigma}$$

and

$$\mathrm{H} = \frac{\mathrm{P}\,.\,76\,.\,\sigma}{\mathrm{S}}.$$

By substituting this expression in the above equation, we have—

$$p = p_1 + \frac{\mathrm{P}\,.\,\mathrm{M}\,.\,p_1}{1000\ \mathrm{S}\,.\,0{\cdot}0819\ \mathrm{T}}$$

and for the osmotic pressure we therefore have the expression

$$\mathrm{P} = \frac{p - p_1}{p_1}\,.\,\frac{0{\cdot}0819\ \mathrm{T}\,.\,1000\ \mathrm{S}}{\mathrm{M}}\ \text{atmos.}$$

This equation, however, applies only to very dilute solutions, and a more accurate expression is obtained in the following manner:—If, by a suitable exertion of power, we move the semi-permeable plunger, in Fig. 14, Plate I., downwards to an extent equal to the volume dv, we shall press out from the solution dx gram-molecules of the solvent, and thus have done an amount of work equal to $\mathrm{P}\,.\,dv$.

Had the same quantity of the solvent been withdrawn from the solution by (isothermal) distillation, the amount of energy consumed would have been—

$$dx\,\mathrm{R\,T}\,.\,l\,.\,\frac{p}{p_1}$$

which evidently must be quite as great as in the former case. Hence we should have—

$$P \cdot dv = dx \cdot R T \cdot l \frac{p}{p_1}$$

and

$$P = \frac{dx}{dv} \cdot R \cdot T \cdot l \frac{p}{p_1}.$$

If no alteration in volume or expansion occur on the mixing of the solvent and dissolved body—which is approximately the case, even with 30 per cent. solutions—then the volume of the liquid will, by the addition of dx gram-molecules of the solvent, be increased by—

$$dv = \frac{M}{S} dx.$$

We can therefore substitute in the above equation—

$$\frac{dx}{dv} = \frac{S}{M}$$

and thus obtain

$$P = \frac{S}{M} \cdot R T \cdot l \frac{p}{p_1}.$$

By substituting $R = 0{\cdot}0819$, and expressing the volume of a gram-molecule in litres, we finally arrive at the expression—

$$P = \frac{0{\cdot}0819\ T \cdot 1000\ S}{M} l \cdot \frac{p}{p_1} \text{ atmos.}$$

2. As we have seen, the vapour tension of a solvent is lowered by the presence of the dissolved substance, *i.e.* the pressure being equal, the boiling point is raised.

In order to determine the connection between the increase of boiling point (when small) and the osmotic pressure, use may be made of the formula of Clausius—

$$\frac{dlp}{dT} = \frac{\lambda}{R T^2}$$

wherein λ = the molecular heat of vaporisation, the integration of which formula furnishes the expression—

$$lp = -\frac{\lambda}{R T} + \text{const.}$$

The equation $l p_0 = -\frac{\lambda}{R T_0} + \text{const.}$ applies to the boiling point T_0 of the pure solvent, and therefore—

$$l \frac{p}{p_1} = l \frac{p}{p_0} = \frac{\lambda}{R} \left[\frac{1}{T_0} - \frac{1}{T}\right].$$

By substitution in the previous equation—

$$P = \frac{0{\cdot}0819\ T . 1000\ S}{M} l \frac{p}{p_1}$$

we have $P = \frac{0{\cdot}0819\ T . 1000\ S}{M} \cdot \frac{\lambda}{0{\cdot}0819} \left[\frac{1}{T_0} - \frac{1}{T}\right]$.

If we express herein the latent heat of vaporisation of 1 grm. of the solvent by $l = \frac{\lambda}{M}$ and substitute $t = T - T_0$, we have $P = \frac{T . 1000\ S . l . t}{24{\cdot}17\ T_0 T} = \frac{1000\ S . l . t}{24{\cdot}17\ T_0}$ atmos.

wherein 24·17 represents the equivalent of a litre-atmosphere in gram-calories.

3. It is a well-known fact that substances vaporise from the solid state as well as when in the liquid condition. The freezing point of a liquid is, however, the temperature at which the two conditions—solid and liquid—of the same body can exist at the same time, and, as a simple observation will show, the vapour tension of the liquid body at the freezing point must be just as great as that of the solid substance, since otherwise one of the two conditions of aggregation would vaporise more rapidly than the other, in which event the equilibrium between the solid and the liquid condition would suffer disturbance, *i.e.* the two forms could not exist side by side.

As now the vapour tension of the liquid solvent is depressed by the addition of a foreign body, that of the solid solvent must also suffer reduction at the freezing point, or, in other words, the freezing point of a solution must be lower than that of the pure solvent.

With reference to the molecular heat of vaporisation, we have already made acquaintance with the Clausius equation $\lambda = R T^2 \frac{d . l p}{d T}$. Similarly, for the molecular heat of sublimation of the solid body, we have $\sigma = R T^2 \frac{d l p_1}{d T}$, wherein p implies the vapour tension of the liquid solvent, and p_1 that of the solid solvent, both at the freezing point. From this we obtain by integration—

$$l p = -\frac{\lambda}{R T} + C'$$

and

$$l p_1 = -\frac{\sigma}{R T} + C.$$

Now, as we have already seen that $p = p_1 = p_0$ at the freezing point, we may write—

$$l p_0 = -\frac{\sigma}{R T} + C'$$

$$l p_0 = -\frac{\lambda}{R T} + C.$$

Hence it follows that—

$$l p_1 - l p_0 = l \frac{p_1}{p_0} = -\frac{\sigma}{R T}\left[\frac{1}{T} - \frac{1}{T_0}\right]$$

$$l p - l p_0 = l \frac{p}{p_0} = -\frac{\lambda}{R T}\left[\frac{1}{T} - \frac{1}{T_0}\right]$$

and, by subtracting one equation from another, we obtain—

$$l \frac{p}{p_1} = \frac{\sigma - \lambda}{R T}\left[\frac{1}{T} - \frac{1}{T_0}\right].$$

If we express the molecular heat of fusion of the solvent by $w = \sigma - \lambda$, and the heat of fusion in gram-calories, then (in analogy with the boiling-point equation) we obtain—

$$P = \frac{1000 S . w}{24{\cdot}17} \cdot \frac{t}{T_0} \text{ atmos.}$$

wherein t indicates the lowering of the freezing point.

According to the foregoing, the presence of a second constituent of a solution raises the boiling point of the first constituent, but lowers the solidification point. In the second chapter, however, we made the acquaintance of solutions, wherein, on the contrary, the solidification point of the one constituent of a solution is raised by the presence of a second: of this class are the solutions of such bodies, which together furnish a homogeneous mixture.

In order to understand this behaviour we will investigate the vapour tension of solutions consisting of two volatile components, and in observing these phenomena will follow the clear description given by W. Nernst.

When to a liquid, A, a small quantity of a second, B, is added, the result is, on the one hand, to diminish the vapour tension of A, whilst on the other hand the total vapour pressure of the resulting solution is increased by the circumstance that the dissolved quantity of B also evolves vapour; in fact, the partial pressure of B in the vapour in a state of equilibrium with the resulting solution is the greater in proportion as the coefficient of solubility of the vapour of B is smaller as regards the liquid A. The same naturally applies to solutions formed of small additions of A to B, which also may, according to circumstances, have a larger or smaller vapour pressure than the liquid B by itself. As now the properties of the mixture must vary in accordance with its composition, a distinction will have to be drawn between the three following typical cases as regards the dependence of the vapour tension on the mutual ratio of the two liquids:—

"I. The vapour of A is readily soluble in B, and the vapour of B in A. Then, whether the addition consist of a small quantity of A to B, or of B to A, the vapour tension of the resulting solution will decrease. Starting with the solvent A, the vapour pressure of which we will assume to be p_1, at the prevailing temperature, and adding thereto successively

increasing quantities of B, the vapour pressure will decrease at first, until a minimum is attained, whereupon it reascends, and finally, in the presence of very high proportions of B, approximates to the vapour pressure of the pure solvent, namely, p_2.

"II. The vapour of A is but slightly soluble in B, and that of B in A. In this event the addition of a small quantity of A to B, or of B to A, will increase the vapour tension of the resulting solution. Consequently, given successive additions of B to A, the vapour pressure of the solution will at first be greater than p_1, thereafter attaining a maximum, and finally, as there occurs a large excess of B, will recede again and approximate to the value p_2.

"III. The vapour of the one liquid is readily soluble in the other, whereas that of the second is only soluble with difficulty in the first. Under these circumstances a slight addition of B to A will make the vapour tension of the resulting solution smaller than that of the solvent, but a small addition of A to B will raise the vapour tension in comparison with that of the solvent. If now the vapour pressure of A (p_1) be greater than the vapour pressure, p_2, of B, then the result of successive additions of B to A will be to cause the vapour tension of the solution to continuously recede from p_1 to p_2, without attaining any maximum or minimum (III*a*). It is, however, imaginable that, conversely, the initial addition of B to A would increase the vapour tension, whilst the addition of A to B would diminish it; in such event, the result of successive additions of B to A would at first be to cause the vapour tension of the mixture to increase, attain a maximum, then decline until of lower value than p_2, traverse a minimum, and finally, in presence of a large excess of B, approximate to the value p_2 (III*b*)."

The comprehension of this phenomenon will be facilitated by a glance at the curve plotted in Fig. 16 (Plate I.). The

abscissæ represent the proportions of the mixture (percentage of B), the ordinates indicating their vapour tension. For the case No. I., the example selected is a mixture of formic acid and water; for No. II., water and propyl alcohol; for No. III*a*, ethyl- or methyl alcohol and water. On the other hand, the dotted curve representing the case No. III*b* has not yet been discussed or realised.

The case No. III*a* applies to solutions the components of which form homogeneous mixtures.

Strictly speaking, all that has been stated above with regard to osmotic pressure and its relation to the other properties of solutions, applies only to dilute solutions, though the laws in question also apply, in an approximate degree, to higher concentrations as well.

Dieterici (*Wied. Ann.*, 1894, 52, p. 263), as also Th. Evans (*Zeits. f. phys. Chem.*, 1894, 14, p. 409), have shown that, even with higher concentrations, the dimensions of the osmotic pressure remain proportional to the quantity of substance dissolved. For the relation between the osmotic energy and the vapour tension, and the lowering of the solidification point, the former gives the expressions—

$$\Pi = \mathrm{R}.\mathrm{T}.ln\frac{p}{p_1}$$

and

$$\Pi = t\left[\frac{\rho}{\mathrm{T}_0} - \frac{\mathrm{C}_1 - \mathrm{C}_2}{2}\cdot\frac{t}{\mathrm{T}} + \frac{\mathrm{C}_1 - \mathrm{C}_2}{3}\cdot\frac{t^2}{\mathrm{T}^2}\right]$$

or the osmotic energy reduced to the freezing point of the solvent, taken alone—

$$\Pi_0 = t\left[\frac{\rho - q}{\mathrm{T}} - \frac{\mathrm{C}_1 - \mathrm{C}_2}{2}\cdot\mathrm{T}_0\frac{t}{\mathrm{T}^2} + \frac{\mathrm{C}_1 - \mathrm{C}_2}{3}\cdot\frac{t^2}{\mathrm{T}^3}\right].$$

In these equations—

Π equals the osmotic energy,

R, the gas constants,

p, the vapour tension of the pure solvent,

p_1, the vapour tension of the solution,

t, the reduction of the solidification point,

$\rho = \sigma_0 - \lambda_0 + (C_1 - C_2)\, T_1$, the molecular heat of fusion at the temperature T,

σ_0, the latent heat of sublimation of a molecule at the fusing temperature,

λ_0, the latent heat of vaporisation of a molecule at the fusing temperature,

T_0, the melting point of the pure solvent,

C_1, the molecular heat of the liquid solvent,

C_2, the molecular heat of the solid solvent,

q, the heat of dilution.

The values for osmotic energy, calculated from the foregoing equations, are, as the following figures will show in the case of solutions of potassium chloride, actually proportional to the concentration :—

m[1]	t	q	p^1	Π_0	
				Cal. 1.	Cal. 2.
0	0	0	4·620	...	...
3·72	1·667	- 1·63	4·546	8·80	8·75
7·45	3·284	- 5·96	4·472	17·55	17·67
14·90	6·53	- 19·5	4·326	35·18	35·71
22·35	9·69	- 34·3	4·190	52·64	53·12

[1] Percentage of KCl in the solution.

The first value for Π_0 is calculated from the vapour tension, the second from the depression of the solidification point.

C. T. Heycock and F. H. Neville (*Trans. Chem. Soc.*, 1890, vol. 57, pp. 376–393) have proposed another and simpler method for arriving at equations which shall also apply to concentrated solutions.

On the basis of Lagrange's equation of movement, Professor

J. J. Thomson (*Application of Dynamics to Chemistry and Physics*, p. 263) has deduced the equation—

$$E = \frac{p \cdot T}{s \cdot w}$$

for the molecular depression of the solidification point, in which equation p represents the osmotic pressure and s the density of the solvent; this equation is identical with the $E = 0{\cdot}0198\frac{T_2}{w}$ of van't Hoff.

If, in order to render the above formula clearer, we take as example the case of an alloy of tin and gold, in which the former metal predominates, it will be found that, during the cooling of the alloy, pure tin in the solid form will be the first to separate out, and that the volume in which the gold is distributed is therefore reduced. Consequently the energy p must be exerted in order to overcome the osmotic pressure. When the unit volume of tin solidifies out, the work p has to be performed to compress the gold. A source of this energy is to be found in the liquid, which may be regarded as a perfect caloric machine; since, on the solidification of a unit volume of tin in the pure state at the temperature T, an amount of heat represented by $s \cdot w$ is disengaged. If, however, the tin solidifies at $T - t$, then, according to Carnot's law, a portion of this heat (namely, $\frac{t}{T} \cdot w \cdot s$) is converted into work.

If we pose this expression $= p$, we obtain—

$$p = \frac{t}{T} \cdot w \cdot s$$

or—

$$t = \frac{T \cdot p}{w \cdot s}$$

wherein t indicates the reduction of temperature which must ensue before the necessary amount of energy can be exerted.

In the case of a solution of 1 mol. of a metal in 100 atoms of tin, we have—

Melting point of tin = 231°·5 C. or 504°·5 absolute,

w = 14·25 cal. (Person) = $14{\cdot}25 \times 41{\cdot}6 \times 10^6$ dynes,

s = 7·29,

Sn = 118 (atomic weight of tin).

Hence the volume of a solution containing 100 atoms of tin is equal to $\frac{100 \times 118}{1000 \,.\, s} = \frac{11{\cdot}8}{s}$ litres, and the solidification temperature can be approximately gauged at 500° absolute. In this way we ascertain the osmotic pressure, called into action by the presence of a molecule of an extraneous metal, to be—

$$p = \frac{\Pi \times 22{\cdot}3 \times 500 \times s}{11{\cdot}8 \times 273} = 3{\cdot}46\ \Pi \,.\, s,$$

$\Pi = 1013 \times 10^3$ dynes representing the atmosphere pressure. By substituting this value in the formula $t = \frac{\mathrm{T} \,.\, p}{w \,.\, s}$, the molecular depression of the melting point works out as E = 3° C. (A more precise calculation gives p = 3°·5, and t = 4°·14 C., whereas the van't Hoff equation gives—

$$\mathrm{E} = 0{\cdot}0198 \frac{\mathrm{T}^2}{w} = 3°{\cdot}54 \text{ C.})$$

The above-mentioned equation of J. J. Thomson can also be made applicable to more concentrated solutions, by bearing in mind that p does not vary as T but as $\mathrm{T} - t$, and that the volume of the solution is greater than that of the original solvent. In this case we have—

$$\mathrm{E} = \frac{0{\cdot}0198\ (\mathrm{T}-t)^2}{w} = \frac{p}{w \,.\, s}(\mathrm{T}-t)$$

and

$$p = s \,.\, w \frac{\mathrm{M}}{m} \cdot \frac{t}{(\mathrm{T}-t)}$$

wherein s is the density of the molten solution, w the latent

heat of fusion of the solvent, M the molecular weight of the dissolved body, m the proportion of dissolved substance per 100 parts of solvent, t the depression of the melting point, and T the melting point of the solvent in absolute temperature.

CHAPTER V

OSMOTIC PRESSURE AND MOLECULAR WEIGHT OF THE DISSOLVED SUBSTANCE

In the third chapter we learned the axiom that the osmotic pressure of a dissolved body is just as great as the pressure which would be exerted by the same substance were it occupying, in a gaseous state, the same space as the solution, at the existing temperature.

Now since, according to Avogadro's law, equal volumes of all gases at the same temperature and pressure contain an equal number of molecules, it follows therefore that under these circumstances the density of the gases must be proportional to their molecular weights, and the same must also apply to solutions which at equal temperatures exhibit equal osmotic pressure, and are therefore isosmotic.

Hence the osmotic pressure affords a means of determining the molecular dimensions of the dissolved substance, and is actually employed for this purpose, frequently with advantage.

For instance, if a solution contain c grms. of the dissolved body per litre, and exhibits the osmotic pressure p (in atmos.), its molecular weight will be—

$$M = 22{\cdot}41\,(1 + 0{\cdot}00367\,t)\,\frac{c}{p}$$

since the gram-molecule—or, as it is usually termed, the mol.—of a substance exerts a pressure of 22·41 atmos. when enclosed in one litre at 0° C.

Now, as it is but seldom that the osmotic pressure can be measured direct, the equations employed for the calculation of the molecular weight are referred, not to this, but to the depression of the vapour tension, the elevation of the boiling point, or to the depression of the solidification point of the solution.

This last-named method is the only one applicable in the case of alloys, and on this account will be the only one more closely described here.

If we represent by E the molecular depression of the freezing point sustained by the solvent in question, *i.e.* the depression of freezing point sustained by a solvent in consequence of the dissolution therein of 1 mol. of a given substance per 100 grms.; and if we take m to indicate the quantity of the said substance dissolved in 100 grms. of the said solvent, the depression of the freezing point being expressed by t, then the molecular weight of the first will be—

$$M = E \frac{m}{t}.$$

By means, however, of the gas constants R and the temperature of fusion T_0 expressed in absolute figures, the value of E and the heat of fusion w of the solvent can be calculated by the equation—

$$E = \frac{R \cdot T_0^2}{100w}.$$

If we calculate w in calories, then R also must be expressed in the same way, and we obtain—

$$E = \frac{0{\cdot}01991 \cdot T_0^2}{w}.$$

On the other hand, for concentrated solutions, use may be made of the equation $M = \frac{0{\cdot}0198m\,(T-t)^2}{w \cdot t}$ of Heycock and Neville.

Now it has been shown that the molecular dimen[illegible]

the dissolved substance depend on the nature of the solvent and the concentration of the solution. Thus, for example, it is found that the molecular weight of acetic acid when dissolved in benzol (not too dilute) is 120 (corresponding to the formula $(CH_3COOH)_2$), whilst when in solution in ether it is only 60 (corresponding to the formula CH_3COOH), and when dissolved in water is still smaller. In the latter condition it must therefore be dissociated. Consequently the solvents can be arranged in order, according to their "power of dissociation."

The greatest action in this particular is exerted by water, after which solvent can be arranged a series of others exhibiting this power in a minor degree. Alcohols, phenols, esters, ether, and acetone have only low powers of dissociation, and, when the concentration is not too great, the dissolved substances exhibit normal molecular weights; on the other hand, anethol, azobenzol, paratoluidin, and still more, benzol, naphthalene, diphenylmethane, diphenyl, carbon disulphide, chloroform, ethylene bromide, etc., show a more or less pronounced tendency to unite the dissolved substance to form higher molecular complexes—double molecules in particular.

In a given solvent the tendency to dissociation increases with the degree of dilution, as will be evident from the following figures relating to solutions of chloral hydrate in glacial acetic acid—

m	t	a
0·266	0·095	0·52
1·179	0·385	0·38
2·447	0·755	0·31
4·900	1·450	0·25

In this table m expresses the number of grams of chloral hydrate dissolved in 100 grams of glacial acetic acid; t is the

depression of the freezing point, and a the "degree of dissociation," *i.e.* the proportion of dissociated molecules referred to 1 gram of chloral hydrate.

The cause of this power of dissociation is still unknown, but it would appear to increase with the dielectrical constant. Perhaps the solvent exerts some chemical action on the dissolved substance.

Nernst (*Theoretische Chemie*, second edition, p. 262) expresses himself on this point as follows:—"The solution of this question has engaged a good deal of attention, but so far without any successful result. It must be emphasised that if any combination does occur between the solvent and the dissolved substance present in a solution of low concentration, it does not in any way alter the number of dissolved molecules, and therefore does not change the osmotic pressure of the latter; therefore it cannot find expression in the values obtained in respect of the depression of the freezing point, etc."

This view needs correcting in one particular, inasmuch as though the number of molecules of a substance dissolved in a given weight of a solvent does not undergo any alteration in consequence of a chemical combination being formed between that substance and the solvent, nevertheless the relation between solvent and dissolved substance sustains an alteration which, under certain circumstances, justifies us in concluding that such combination has occurred. This is decidedly the case when solutions of elements are in question, and when the molecular weight of the dissolved element, as deduced from the depression of the freezing point, comes out smaller than the atomic weight. If the particulars as to the melting point and latent heat of fusion are reliable, there is then no other course open than the foregoing assumption, unless we assume a subdivision of the atom.

Thus, for example, in the case of alloys of tin with lead and bismuth, we have—

Composition.			Fusing Point.	t	m	M	n
Sn	Pb	Bi	°C.				
100	...	...	232·7	...	...	...	...
90	10	...	210	22·7	11·11	180·495	0·874
90	...	10	210	22·7	11·11	180·495	0·860

Here n expresses the average number of atoms constituting the molecule, whilst the other letters refer to the same particulars as before.

If we assume, in both cases, the combination of 1 atom of tin with 1 atom of lead or bismuth, then we should have—

Composition.			Fusing Point.	t	m	M	n
Sn	Pb Sn	Bi Sn	°C.				
100	...	...	232·7	...	...	...	...
84·25	15·75	...	210	22·7	18·69	305·4	1·88
84·28	...	15·72	210	22·7	18·65	303·0	1·86

On the other hand, the assumption that 2 atoms of tin have combined with 1 atom of lead or bismuth, would give—

Composition.			Fusing Point.	t	m	M	n
Sn	$PbSn_2$	$BiSn_2$	°C.				
100	...	...	232·7	...	...	...	...
78·5	21·5	...	210	22·7	27·51	476·6	3·21
78·56	...	21·44	210	22·7	27·29	473·0	3·18

that is to say, values that are quite possible from the standpoint of theoretical chemistry.

If this behaviour should be confirmed by subsequent investigation, a plausible explanation of the dissociating power of certain solvents would be afforded.

In many cases it can be demonstrated chemically that, during the cooling of solutions, the solvent does not separate out in a pure state. In such cases the assumption that combination has occurred between solvent and dissolved substance would appear correct; nevertheless, this behaviour can also be explained by the so-called "phenomena of adsorption."

Thus, for instance, if powdered wood charcoal be shaken up along with a solution of iodine, a separation of iodine occurs on the surface of the charcoal, the amount of iodine "adsorbed" in this manner depending on its osmotic pressure in the solution. The assumption of the formation of a solid solution is here out of the question, the equilibrium of adsorption being established with a rapidity incompatible with the rate of diffusion in solid substances during the formation of such a solution.

As is evident from the foregoing, the molecular weight of the dissolved substance can only be deduced with certainty from the depression of the solidification point, provided the other constituent of the solution separates out in a pure state.

If this is not the case, we may frequently arrive at a correction of the value, or at a more accurate opinion as to the form in which the dissolved substance is present in the solution, by obtaining figures for the molecular weight that are impossible according to the formula. Nevertheless, such deductions must be confirmed by other investigations if they are to be accepted as certain.

If the chemical composition of the separated constituent

be known, and is constant in the case of dilute solutions, the calculation of the molecular weight may be performed by adding to the solvent the composition of the separated components, and deducing therefrom the value of m. Of course the corresponding values for the melting point and the latent heat of fusion must also be taken into account.

CHAPTER VI

SOLUTIONS OF GASES

ALL liquids, and some solid bodies, possess the property of dissolving gases. The quantity of gas that can be taken up by any liquid depends on the nature of the gas as well as on that of the liquid itself, and for any given gas and liquid is proportional to the gas pressure (Henry's law). If we call the amount of gas contained in unit volume of the gas itself, and in that of the liquid, its concentration (volumetric), it may also be said that, for the gas and liquid in question, the concentration in gas volume is also in the same proportion to that in liquid volume when the pressure changes. This constant ratio of the concentrations is termed the coefficient of solubility of the gas.

The solubility of a gas in a liquid—consequently the value of its coefficient of solubility—generally diminishes with the temperature.

Gaseous mixtures dissolve in liquids in such a manner as though each portion of the mixture were present alone under its partial pressure (Dalton's law).

All these laws—just as the laws of gases—apply in a merely approximate manner, and the more completely in proportion as the solubility is lower and the pressure less. However, in the case of gases which are exceedingly soluble —to an extent equal to several hundred times the volume of the liquid—the amount of absorbed gas usually increases

at a much slower rate than the pressure, a condition that, however, is mostly attributable to chemical reactions between the solvent and the gas. Occasionally deviations from Henry's law, occurring at low temperatures, disappear when the temperature is raised.

One noteworthy feature is that, when a solution has been saturated with gas at a given pressure, the evolution of gas does not begin immediately on the pressure being lowered. Solutions of gases very readily remain supersaturated, and the removal of the excess of gas only begins when the liquid is brought into intimate contact with the same gas (or, better still, another gas) under reduced pressure. (Energetic agitation, introducing porous powdered substances enclosing a large amount of air, etc.)

The molecular theory of the solution of a gas in a liquid has been stated in a very lucid manner by Ostwald in the following terms:—

"When the molecules of the first-named encounter the surface of the water, they are held fast in consequence of the mutual reaction set up between themselves and the molecules of water. When a certain number of molecules of the gas have been taken up, it will come to pass that also a molecule of gas present in the water will disengage itself from the attraction thereof, and will return to the space occupied by the gas. This occurrence will be repeated the more frequently the larger the number of gas molecules in the liquid, and finally a state of equilibrium will arise, wherein just as many molecules will enter the liquid as issue therefrom. When the pressure is changed, the number of encountering molecules increases or diminishes in the same ratio; equilibrium, therefore, can only exist when the number of the molecules escaping from the liquid, or the number of those dissolved in the liquid, is changed in equal proportions. Consequently the amount of gas dissolved must be proportional to the pressure.

"In the case of gaseous mixtures, the equilibrium will be established for each component in proportion to the number of its molecules, *i.e.* its partial pressure, independent of the other components, inasmuch as the number of entering and escaping molecules must be the same in each case. That is Dalton's law.

"The influence of temperature changes the number of the ingoing and outcoming molecules in a similar direction, so that at first it remains without effect. At the same time, however, the constitution of the liquid and the mutual reaction of its molecules with those of the gas undergo change, the latter decreasing as the temperature rises. To these latter constituents is largely due the decrease of solubility generally observed with increasing temperature."

For our purpose another phenomenon is of particular interest, namely, that the solubility of gases in liquids is generally diminished by the presence of a dissolved solid body. It must also be mentioned that the solution of gases in liquids is invariably attained by evolution of heat.

CHAPTER VII

SOLID SOLUTIONS

HITHERTO we have considered liquid solutions exclusively. A series of facts, however, compels the assumption that solutions also exist in the solid condition of aggregation.

Thus, for example, iron is capable of absorbing hydrogen, which may even penetrate right through the metal. Platinum or palladium also absorb considerable quantities of hydrogen, which gradually distributes itself through the whole of the metal.

Solid carbon is capable of penetrating glowing iron, and even of traversing porcelain crucibles, etc. The sole assumption by which these phenomena can be satisfactorily explained, is that solid bodies also possess solvent powers; that consequently solid solutions exist; and this assumption is confirmed by the behaviour of solid alloys in cooling down from a high temperature. In some alloys it is found that, even after complete solidification, they exhibit critical points attended with the evolution of heat.

These critical points,[1] however, as we have seen, afford proof that alterations in condition occur within the alloys at the temperatures in question, and are accompanied by a liberation of energy.

In many instances it has been found possible to show the

[1] The determination of the critical points of alloys, which at the present time forms an important branch of the testing of metals, has received the somewhat peculiar name of "cryoscopy."

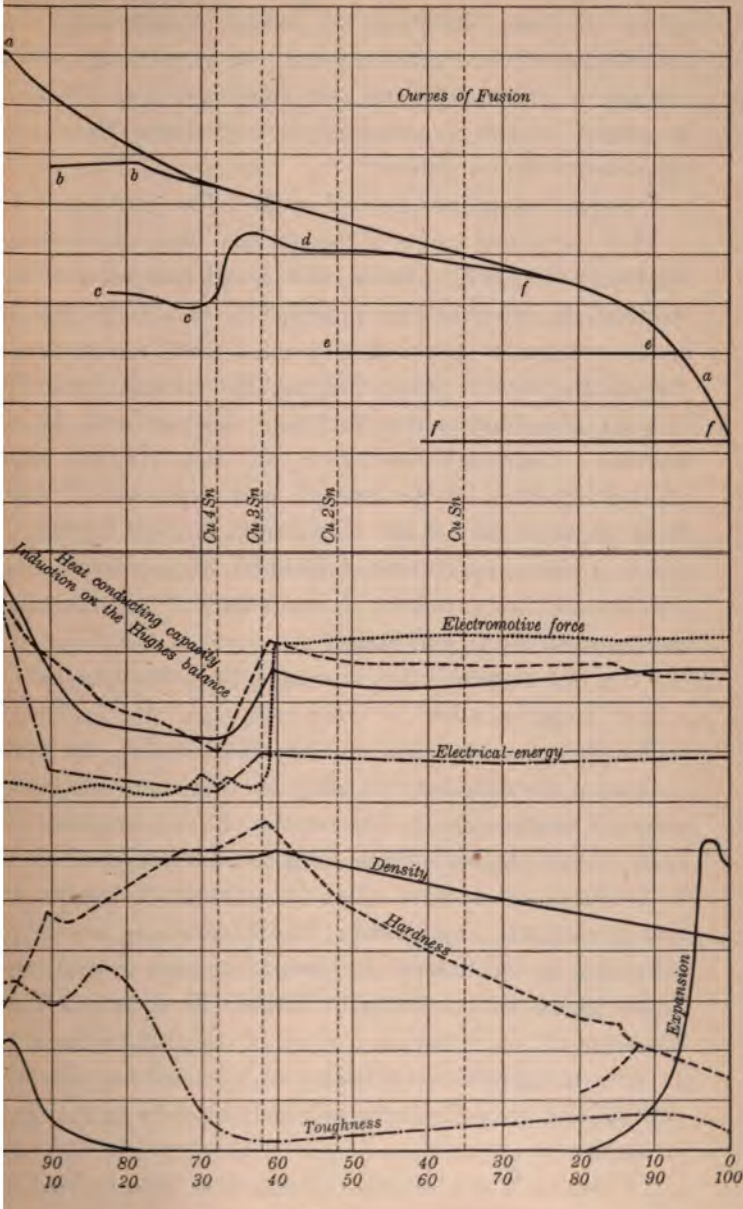

Curves of Fusion
a
b
b
c
c
d
e
e
f
f
f
a
Cu 4 Sn
Cu 3 Sn
Cu 2 Sn
Cu Sn
Heat conducting capacity
Induction or the Hughes balance
Electromotive force
Electrical-energy
Density
Hardness
Expansion
Toughness
90 10
80 20
70 30
60 40
50 50
40 60
30 70
20 80
10 90
0 100

FIG. 17.

nature of these alterations by means of microscopical and microchemical researches. As example, let us take the case of bronzes, of which, it is true, our knowledge is still somewhat imperfect, but which, however, clearly shows the complex character of the conditions.

Osmond[1] expresses himself in the following terms:—

The complete curve of fusion has been determined by Stansfield (Fig. 17). Below this are drawn several curves showing the modifications produced by chemical composition and a number of physical properties, such, for instance, as the electro-motive power (Lanne), the electric conductivity (Lodge), the conductivity for heat (Calvert and Johnson), hardness (Martens), induction on the Hughes balance (Roberts-Austen), tensile strength and expansion (Thurston). Most of these curves are taken from a work by Stansfield. A few, I think, apart from individual irregularities, seem to demonstrate the existence of compounds of definite composition, such as $SnCu_3$ and $SnCu_4$.

By investigating the microstructure, H. Behrens found a still larger number of compounds, and H. Le Chatelier claims to have isolated a compound $SnCu_3$ by rational analysis. Nevertheless, an alloy so composed exhibits two points of recalescence. As a matter of fact, however, almost every one of the conclusions from one set of experiments can be confuted, or at least called in question by the results of another set, and any attempt to explain these variations of behaviour is encountered by insurmountable difficulties. A single glance at the curve of fusion will show the complex character of the question. Some of the alloys have three or four modification- (critical-) or solidification points, the position, and even the curve, of which depends on the rapidity of cooling.

Fortunately the solution of the task may be consider

[1] *Baumaterialkunde*, ii. p. 69.

feasible, thanks mainly to micrographical analysis, which furnishes as many equations as unknown quantities, and with which Guillemin, Behrens, and Charpy have obtained such interesting results. The solution is only a matter of time, patience, and method.

Osmond has described a series of micrographical points taken by Guillemin.

The first series of experiments deals with bronzes which were cast in moulds in the form of square rods of 15 × 15 mm., and contained an amount of tin ranging between 9 and 33 per cent. All the photographs are magnified 100 times, no further details being shown by additional magnification.

The bronze containing 9 per cent. of tin (Fig. 18, Plate II.) appears homogeneous, or at least the examination points to that condition. It probably possesses only a single fusing point, since with this percentage of tin the line *b b* of the second solidification point of Stansfield's curve ceases (according to more recent observations it extends as far as 5 per cent. of tin).

The bronzes with 11, 16, and 19 per cent. of tin (Figs. 19, 20, 21, Plate II.) exhibit, in increasing proportion, a second body, which deposits around the crystals of the first one. Its solidification point is probably indicated by the line *b b* of the diagram.

With 33 per cent. of tin the alloy again becomes homogeneous, and consists of contiguous polyhedra, though in no wise a compound of definite composition ($SnCu_3$ or $SnCu_4$) (Fig. 22, Plate II.).

Another series of photographs shows the influence of the rate of cooling on a bronze containing 19 per cent. of tin. A sample was cast in sand and slowly cooled (Fig. 23, Plate II., magnification 100 diameters). The crystals of the first exhibit more clearly defined shapes than those

of a similar specimen cast in a metal mould (Fig. 21, Plate I
In addition, the matrix, which corresponds to the seco
solidification point, is no longer homogeneous, having sp
up into two constituents, one of which has become colour
by oxidation, as may be seen from the highly magnifie
photograph (Fig. 24, Plate II., magn. 500-fold).

A second sample of the same alloy at dark red he
was hardened in water at 50° C. On examining th
structure (magn. 100-fold linear) it appears to be th
same as above (Fig. 25, Plate II.). However, whe
magnified 500 times linear (Fig. 26, Plate II.), it
seen that the matrix corresponding to the second solidifica
tion point has not split up into two parts. The alteratio
retarded by hardening is probably that corresponding to th
line C C of the diagram. Consequently the line C C appear
less to indicate the true solidification point of a liquid tha
the refining of a so-called solid solution.

Apparently the matrix itself still continues to constitut
a solid solution, which is not dissociated until subjected t
further gradual cooling.

This example illustrates the remarkable analogy existin
between liquid and solid alloys, and shows that many soli
alloys must actually be regarded as solutions.

Under these circumstances these solid solutions must als
follow the laws relating to osmotic pressure, and the relatio
between the temperature of deposition (refining temperature
and molecular weight of the dissolved substance, just th
same as liquid solutions. The sole difference manifested
that the depression of the temperature of conversion do
not in general correspond to the difference between this a
the fusing point of the pure solvent, and that consequent
another value must be substituted for E (the molecular d
pression of the fusing point) in the calculations. This mat
will be dealt with later on.

As we have already seen, the usual procedure during the ooling down of a dilute liquid solution, is for the pure solvent) separate out first, in the solid form, which case we have tilised for the determination of the osmotic pressure, or the olecular weight of the dissolved substance. Now and again, owever, it happens that in such cases the separation that ccurs is not of the pure solvent, but a crystallisation of a olecular mixture of the solvent and the dissolved substance, condition which—apart from chemical examination—can be ecognised by the depression of the solidification point being naller than is furnished by calculation from the molecular veight and the percentage of dissolved substance. Van't Hoff explained this remarkable phenomenon by the assumption that the mixture that crystallises out is a solid solution, hypothesis confirmed by the thorough researches of van Bijlert (*Zeits. f. phys. Chem.*, 1891, vol. viii. p. 343). The atter found, in the case of a solution of thiophene in benzol, hat a solid solution of about one-seventh the concentration f the liquid solution separates out; that in the case of olutions of antimony in tin, or of β-naphthol in naphthaene, a raising of the solidification point ensues; and that n these cases the separated solid solution is of higher concentration than the residual liquid solution.

In the case of gases dissolved in solid bodies, the osmotic pressure must evidently be equal to the gas pressure. *e.g.* (according to van't Hoff) when hydrogen is dissolved in palladium to form Pd_2H.

When a substance distributes itself in constant proportion between a fluid and a solid solvent, the osmotic pressure, referred to equal volumetric concentrations, is equal in both solutions; which agrees with what van Bijlert found in the ase of solutions of thiophene in solid and liquid benzol. This matter will be reverted to in the next chapter.

Mention must here be made of another circumstance. It

not infrequently happens with solid solutions that internal separations or depositions occur, which therefore stand in no relation to a transition from the liquid to the solid condition. Now Victor Rothmund (*Zeits. f. phys. Chem.*, 1897, pp. 705–720) has shown that these depositions are connected with alterations in the molecular condition of the solvent. This worker investigated the alteration sustained by the conversion point of a solid substance on the addition of another body soluble in the first one. The law enunciated by Raoult for liquid solutions, that the relative reduction in the vapour pressure is equal to the molecular concentration of the dissolved substance, was taken as a basis by Rothmund, who arrived at the result that—if the molecular weight is the same in a solid solution during both phases—the alteration of the temperature of conversion is proportional to the concentration of the dissolved substance, but that this proportionality ceases if the molecular weights are different. Consequently the examination of the conversion products at different degrees of concentration affords a means of determining whether the molecular weight of the dissolved substance is the same in both modifications or not. In calculating the molecular weight, however, it is of course necessary to take into consideration the latent heat of conversion of the solvent, instead of the latent heat of fusion

CHAPTER VIII

SOLUBILITY

CONSIDERABLE similarity exists between the phenomena occurring during the evaporation of a liquid, or the liquefaction of a gas, and the solution and deposition of a solid body in and from a liquid.

When a solid body is introduced into a liquid capable of dissolving the same, the former begins—against the laws of gravitation—to distribute through the latter; in other words, to dissolve therein. The process of solution continues until a state of equilibrium is reached, which depends on the nature of the substances concerned and on the temperature.

In the evaporation of liquids, which proceeds in just the same manner, this condition of equilibrium is established when the partial pressure of the vapour present over the liquid is equal to the vapour tension of the liquid itself. Precisely the same applies to solution, inasmuch as here the equilibrium is attained when the osmotic pressure of the dissolved substance reaches the same value as the tension of solution of the solid body, which in turn depends on the temperature and the nature of the substances concerned in the reaction.

This analogy becomes the more remarkable when the two phenomena are regarded from the molecular hypothesis standpoint (the inclusion of the phenomena of fusion and solidification being also appropriate). It is a matter of common knowledge that molecules must not merely be credited with mutual attraction (which also makes itself apparent in the

gaseous condition, and is borne in mind, for instance, in van der Waal's equation of condition), but it must also be assumed that they possess considerable powers of locomotion. The former depends on the average distance between the molecules, and increases considerably as this distance diminishes (according to van der Waal, in inverse ratio to the square of the volume), whilst the locomotive power is dependent on the temperature and mass of the molecules.

In the case of a liquid, the "internal pressure" due to the mutual attraction of the molecules is so great that the mean kinetic force of the molecules is no longer able to overcome it. As a matter of fact, however, this kinetic force is not the same in all molecules, and indeed varies between rather wide limits. If, now, such molecules as have sufficient kinetic energy encounter the surface of the liquid, they will overcome the internal pressure, or the surface tension, escape from the liquid, and move freely, in the same manner as gas molecules, in the overlying space. The number of molecules possessing sufficient kinetic energy for this purpose depends entirely on the temperature. If the space above the liquid be illimitable, then the escaping molecules of vapour move farther and farther away from the liquid, others follow, and the evaporation continues without interruption. The inevitable consequence of this is that the temperature of the liquid is reduced, since only such molecules as possess sufficient kinetic energy, and therefore are of sufficiently high temperature, are able to escape through the surface of the liquid. Hence the molecules left behind in the liquid move at a slower rate, and therefore have a lower temperature. This explains the latent heat of evaporation.

If, on the other hand, the overlying space is restricted, the molecules of vapour cannot escape. In such event they come in contact with the walls, or with other molecules of vapour confined in the same space, and, being thrown back by

these, re-enter the interior of the liquid. In this case, also, a condition of equilibrium must eventually be established, namely, when the number of molecules escaping from the surface of the liquid is equalled by the number returned into contact therewith. The number of the first depends entirely on the temperature, whereas the number of the latter depends on the number of molecules of vapour per unit volume (volumetric concentration) and their velocity (therefore on the temperature also).

If we now pass to the consideration of the transition from the solid to the liquid condition, we must first distinguish between amorphous and crystalline solid bodies. The former may be arranged in one series with liquids, inasmuch as a gradual transition between the two may be demonstrated; the greater the internal friction of a liquid the more viscid it is, and therefore the more nearly does it approximate to the amorphous solid bodies. Conversely, however, amorphous bodies, such as glass, for example, which must undoubtedly be classed as solid, in the ordinary acceptance of the term, exhibit properties entitling them to rank along with viscid liquids. Thus a long glass rod supported at the two ends alone, will gradually bend and become crooked, its parts therefore obeying the influence of gravitation, like liquids do, though more slowly on account of the greater internal friction. This affords a very plausible reason for regarding the amorphous bodies as liquids of high viscosity, an assumption finding additional support in the circumstance that amorphous bodies have no definite melting point; so that the transition from the liquid to the amorphous state may be compared with that of gases into liquids at a greater than the critical pressure.

On the other hand, the crystalline bodies behave in a very different manner. In this case not only must a regular arrangement in the molecule be assumed to occur—in contrast to the case of gases, liquids, and amorphous bodies—but, and

this is a matter of special interest to us, the transition from the liquid to the solid state is accomplished suddenly, *i.e.* any given pressure also corresponds to a certain temperature at which the substance can exist in the liquid and the crystalline state simultaneously. Hence the transition from the former condition to the latter must be classed along with that of a vapour into the liquid condition, below the critical pressure.

The analogy between the two changes of condition extends, however, still further. If a liquid that crystallises on solidifying be left to cool gradually, it, as a rule, will not begin to deposit crystals when the normal temperature of solidification is reached, but becomes more and more viscid, and approaches the amorphous solid state. If, however, it be brought into contact with ever so small a quantity of the same substance in the crystalline state, it immediately solidifies in the form of crystals, the temperature rising up to the melting point, in consequence of the disengaged latent heat of fusion (see the cooling curve for tin in Fig. 27, according to the observations of Roberts-Austen). On the other hand, if crystalline matter be present from the start, no supercooling occurs, but the mass will solidify in a crystalline form at the melting point, and the temperature will remain constant until this solidification is complete throughout.

Vapours may also be supercooled just in the same way, but will condense immediately in presence of even a minute quantity of the same vapour in a condensed state. On the other hand, whilst liquids may also be superheated—in the absence of vapour—without vapour being disengaged, this is impossible in the case of crystalline solid bodies.

A further similarity between the phenomena of vaporisation and melting is the dependence of both the melting point and the evaporation point on pressure. Both temperatures rise as the pressure increases, provided the volume occupied, in the stable condition at higher temperature, is greater than

that filled in the stable condition at lower temperature (which is invariably the case with vapours), whereas under converse circumstances they sink.

The elucidation of these phenomena from the standpoint of the molecular hypothesis has been clearly stated by Ostwald in the following terms:—

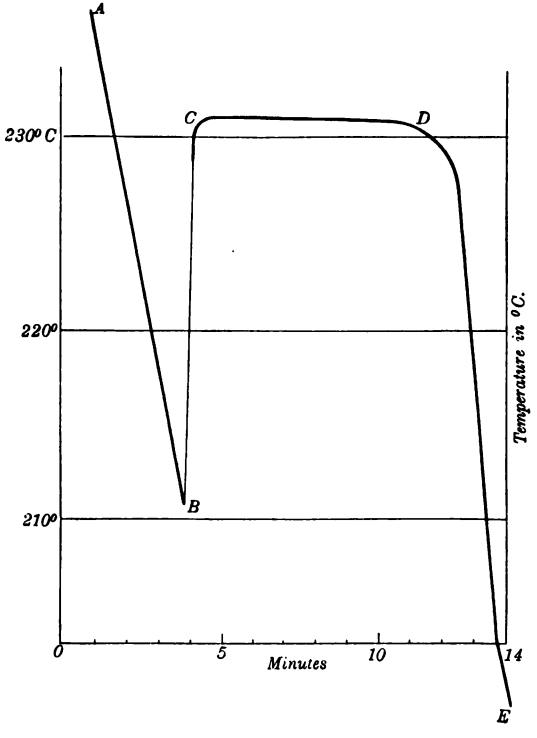


FIG. 27.

In a liquid the molecules move irregularly past one another, and assume any relative position, without exhibiting any preference. A crystal of the same substance introduced into the liquid will liquefy if the temperature be above the melting point, since the kinetic energy of the molecular movement is greater than the force required to disintegrate the crystal.

If the temperature be just that of the melting point, then both values will balance, and just as many molecules will be dissolved from the crystal within a given time as it acquires from the liquid, so that its total dimensions remain unchanged.

Finally, if the temperature be lower, then a smaller number of molecules will be dissolved from the crystal in a given time than it acquires, and consequently the crystal will increase in size.

If, however, the liquid be allowed to cool out of contact with the crystal, there is no impulse given to regular arrangement on the part of the molecules, and supercooling ensues. The kinetic energy of the molecules diminishes, they draw closer and closer together, and it may then happen that, among the numerous collisions of the molecules, there occurs one that throws them just into the regular and particularly stable condition necessary for the production of crystallisation. This gives rise to the circumstances under which the liquid crystallises spontaneously; then ensues a regular deposition of molecules on the crystals so formed, inasmuch as the molecules that come in contact with the crystals in a suitable manner are retained, until the consequent increase of temperature attains the melting point, at which point the number of molecules acquired and released by the crystal are equal.

If a crystal be introduced into the supercooled liquid previous to the commencement of spontaneous crystallisation, the above-described procedure is repeated on that crystal; and if the latter be removed, no further inducement to deposition remains.

The possibility of supercooling evidently depends, therefore, on the ease with which the molecules can accidentally slip into the position of regularity. Consequently liquids of greater fluidity can be much less readily supercooled than

those of a more viscous character; and the larger the quantity of any given liquid the more readily will crystallisation occur, since it is sufficient, for the commencement of crystallisation, that the necessary molecular arrangement is produced at any point in the liquid, and therefore the probability evidently increases in direct proportion to the number of molecules present, *i.e.* with the volume of the supercooled liquid. The possible extent of supercooling in one and the same body therefore differs, and depends on the number of molecules present.

The process of solution of a solid body, or the deposition of such a body from solution, constitutes an additional analogy. If we admit that the dissolved body possesses an osmotic pressure corresponding to the gas pressure, and ascribe to the solid body that is to be dissolved a certain "tension of solution," depending on the temperature and the nature of that body and the solvent, then equilibrium occurs—*i.e.* the solution is saturated—when the osmotic pressure attains an equal value with the tension of solution. Consequently supersaturated solutions are on a parallel with supercooled liquids.

The explanation of the entailed phenomena on the basis of the molecular theory is precisely the same as in the cases of melting and solidification, for which reason we may again quote Ostwald in this place.

As the result of contact between a soluble substance and its solvent, the possibility of moving freely is afforded to its molecules; they pass into the solvent, and this continues until such time as the number of molecules leaving and acquired by the solid body are equal. This evidently depends on the number of molecules present in unit volume of the solution, *i.e.* on the concentration. If the solid body come in contact with a more highly concentrated solution, then a larger number of molecules will be retained by the former than it emits; the solution is "supersaturated," and the

crystal grows.[1] If it be removed, the cause of the deposition ceases to operate, and the solution remains supersaturated. The spontaneous crystallisation of a supersaturated solution is influenced by the same conditions as a supercooled melt.

Naturally, just the same applies to solid solutions as to liquid solutions, and a certain motility of the molecules must also be ascribed to the former.

From what has been already stated, the tension of solution of a solid substance towards a solvent is as great as its osmotic pressure in a saturated solution. According to van't Hoff, the dependence of the tension of solution on the temperature is found from the equation—

$$L = T\frac{dP}{dT}(V - v'),$$

wherein L indicates the quantity of heat absorbed when 1 mol. of the solid substance is dissolved under constant osmotic pressure of the solution saturated at the temperature T. V is the volume of a mol. of the dissolved substance in the saturated solution, v' its volume previous to solution.

Hitherto we have treated of the solubility of a single solid body in a single solvent; it now remains to consider the behaviour of several solid bodies towards one and the same solvent, as well as the behaviour of a single solid body towards several solvents.

The behaviour of several solid bodies, simultaneously present, towards one and the same solvent, may be of varying character.

[1] The term "supersaturated," however, refers solely to solid substances of definite composition. Thus, if a solution of sodium sulphate be cooled down to a low temperature, both $Na_2SO_4+7H_2O$ and $Na_2SO_4+10H_2O$ can be deposited therefrom. Now, since the former salt is far more soluble than the latter, it is evident that a solution can be prepared which, on contact with solid $Na_2SO_4+10H_2O$, will crystallise immediately, and is therefore supersaturated with that salt, although still capable of dissolving small quantities of the salt $Na_2SO_4+7H_2O$, and therefore not fully saturated with this latter. The same solution, however, may be supersaturated for both salts by cooling it down still further.

Some bodies, when brought simultaneously into contact with a solvent, give a solution of definite composition at a given temperature, irrespective of the relative proportions in which they are employed, provided only they are present in excess. Examples of this class are afforded by the nitrates and chlorides of the alkali metals and ammonia, as also by ammonium chloride and barium chloride, sodium chloride and copper chloride, potassium nitrate and lead nitrate, sodium sulphate and copper sulphate, etc.

In other cases, again, the concentration of the resulting solution varies according to the relative proportions of the substances to be dissolved. Such substances either form definite double salts or are isomorphous, the two groups differing in behaviour, as shown by Ostwald. Thus if one of the two constituents of a double salt be dissolved in a solution of such double salt by the aid of heat, and then allowed to crystallise, a diminished proportion of the other constituent will be found remaining in the solution. By repeating the process a solution of constant composition will finally be attained, containing a residual non-displaceable remnant of the salt. A similar result will follow the addition of the other constituent salt in the same manner. Thus, instead of one solution furnished by the grouped substances of the first class, we here obtain two terminal solutions of constant composition, together with solutions containing all the intermediate proportions of the constituents.

As a rule the actual displacement of isomorphous salts is complete if the solution be repeatedly treated with an excess of one of the two salts in the warm, and left to crystallise out.

With bodies of the first group, equilibrium is established between osmotic pressure and the tension of solution of each dissolved body separately, and consequently a separate definite constitution of the solution must correspond with each given

temperature. In the cases of bodies entering into mutual combination, equilibrium is established between the possible compound and the constituent present in excess; hence there must be two stable conditions of equilibrium, corresponding to the three eventualities, that either one or the other, or neither, is in excess. Finally, with isomorphous bodies, any given constitution of the mixture of undissolved substances has its own particular condition of equilibrium, and therefore also a definite composition for the concentrated solution.

The distribution of a substance between two solvents of low mutual solubility proceeds in accordance with the following laws, the term "coefficient of distribution" being applied to the ratio of the volumetric concentration of the substance in the two solvents after the establishment of equilibrium:—

1. If the dissolved substance exhibit the same molecular weight in both solvents, the coefficient of distribution is constant at the given temperature, and therefore the osmotic pressure in the two solutions if the volumetric concentration be equal.

2. If several dissolved substances be present, each separate class of molecules will be distributed as though alone.

3. If the dissolved substance be in a state of dissociation, and not in a uniform molecular condition, law 1 will apply to each of the classes of molecule resulting from the dissociation.

CHAPTER IX

DIFFUSION

It has already been stated that a solid body, in passing into solution, is distributed uniformly through the solution, contrary to the laws of gravitation; the same is also true when two solutions of different degrees of concentration are placed in contact, and it may be stated that, in general, dissolved substances wander from positions of higher concentration to those of lower concentration. This phenomenon is termed "diffusion."

Osmotic pressure is evidently the motive power by which diffusion is effected, and the process itself corresponds exactly to what happens in the course of equalising differences of density in the case of gases, the only point of difference being the rate at which the processes are carried on, the higher internal friction in the case of liquids rendering the operation much slower than with gases.

Now, since the differences in osmotic pressure are proportional to the pressure of concentration, the rate of diffusion must also be proportional thereto (Fick's law). The quantity of dissolved substance that will pass through unit sectional area in unit time at a given temperature, when the difference in concentration between two sectional areas, situated at unit distance apart, is taken as 1, is termed the "coefficient of diffusion." This value depends on the nature of the solvent and the dissolved substance, increases with the temperature, and apparently changes with the concentration.

The coefficient of diffusion being known, and also the osmotic pressure, the frictional resistance K can be calculated by the formula—

$$K = \frac{1{\cdot}99}{D} \times 10^9 \, (1 + 0{\cdot}00367\, t)$$

(Nernst, *Zeits. f. phys. Chem.*, 1888, vol. ii. p. 613).

In this manner it is found, for example, that the displacement of 1 mol. of saccharose (342 grms.) at a velocity of 1 cm. per second, in its aqueous solution, at 18° C., requires a force of traction equal to 4,700,000,000 kilos.

From the rate of diffusion of dissolved bodies, and the mean velocity of their molecules, u (in accordance with the kinetic theory of gases), Riecke deduces the dimensions of their mean free path traversed (in mm.), and finds—

$$L = \frac{3\,D}{8{\cdot}64 \times 10^4 u}.$$

Now similar phenomena of diffusion appear also in the case of metallic alloys, and we will therefore consider certain of them here, although—so far as iron is concerned—they will be more fully dealt with in a later section.

The question has often been posed why it is that a uniform mass results on cooling, when two metals have been fused together, or a fresh metal has been added to an existing melt consisting of two or more metals. For instance, if a few kilos. of ferromanganese be added to 10 tons of molten iron in a converter, the resulting ingots will be of fairly uniform composition. It is true that partial spontaneous separation may disturb the uniformity of distribution in each individual ingot, to a certain extent, but the percentage of manganese in each ingot will be approximately the same throughout. This uniformity cannot be entirely due to the mechanical movement of the molten mass within the converter, and we are therefore constrained to attribute a certain power of motility to the molecules of metal. This applies

to a number of alloys, and in studying those molecular movements it will be preferable to select such alloys as do not suffer disturbance, in point of uniformity of distribution, through the influence of spontaneous separation. Graham has shown that this molecular motility, in the case of saline solutions, increases considerably with the temperature; consequently, in investigations of this kind, particular attention must be paid to the temperature at which the diffusion occurs.

On this point a series of very interesting researches has been published by Roberts-Austen (*Phil. Trans. Royal Soc.*,

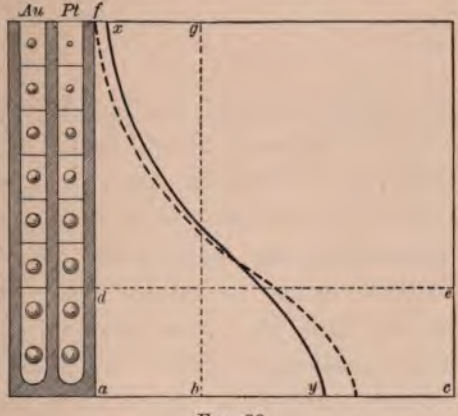


FIG. 28.

1896, clxxxvii. A., p. 383), which may be briefly recapitulated here. This worker inserted the different metals under examination into the bottom of tubes filled with molten lead (the tubes being heated to 500° C. for twenty-four hours, side by side). The results of the experiment are plotted in Fig. 28, the strips marked Pt and Au showing the actual dimensions of the two lead cylinders. The inscribed circles represent the quantities of gold and platinum found in the different sections of the lead cylinders after solidification. The adjacent curves relate to the path traversed during diffusion, as ordinates, and the concentration, as abscissæ.

The following table gives a view of the results obtained:—

Diffusing Metals.	Solvent Metal.	Temperature, ° C.	Relative Diffusibility in 24 Hours.
Gold	Lead	492	3·00
,, ...	,,	492	3·07
Platinum	,,	492	1·69
,, ...	,,	492	1·69
Gold	,,	550	3·18
Rhodium	,,	550	3·03
Gold	,,	555	3·19
,, ...	Bismuth	555	4·52
,, ...	Tin	555	4·65
Silver	,,	555	4·14
Lead	,,	555	3·18

It is thus evident that gold and bismuth diffuse more rapidly in tin than in the heavier metal lead.

Other experiments have shown that a measurable degree of diffusion occurs in solid as well as in molten metals. It is certainly noteworthy that gold, when placed under a cylinder of lead, 3 inches in height, and exposed to a temperature of only 200° C., *i.e.* far below its fusing point, should diffuse in considerable quantity as far as the top of the cylinder within three days. Even when the lead was heated to only 100° C., the gold diffused in measurable quantities, though 100,000 times less than in molten lead.

The diffusibility of one metal in another is therefore quite as measurable a quantity as electrical conductivity. The figures in the final column of the foregoing table give the number of grains of diffused metal traversing 1 sq. cm. of tube section in twenty-four hours, when the difference in the content of the resulting alloy reaches 1 grain per c.c. for each 1 cm. of longitudinal distance. The coefficients of diffusion are found by multiplying these figures by—

$$\frac{15{\cdot}43}{24 \times 60 \times 60} = 0{\cdot}000178.$$

With regard to the mutual diffusion of solid bodies, it should be mentioned that this power has long been known and utilised for industrial purposes: for example, the penetration of carbon into solid iron during the cementation process.

CHAPTER X

ELECTRICAL CONDUCTIVITY: CONSTITUTION OF ELECTROLYTES AND METALS

In point of electrical conductivity a sharp distinction may be drawn between electrolytes and metals, the conduction of the electric current resting in the former case on a conveyance of material, whilst this is not so in the case of metals.

Pure hydrochloric acid gas is just as poor a conductor as pure water, whereas an aqueous solution of hydrochloric acid forms a good conductor, free chlorine being then deposited at the positive pole (anode) and free hydrogen at the negative pole (kathode). Now this can only occur when the chlorine in the solution travels in one direction, and the hydrogen in the opposite direction; and the simplest explanation is afforded by the assumption that the electrolyte consists of parts of different polarity, *i.e.* of molecules (also called "ions") laden with positive, and others laden with negative, electricity. The electric (galvanic) current is then set up by the positive ions (kathions) wandering in the direction of the positive current, and the negative ions (anions) in the direction of the negative current.

This assumption finds important confirmation in the previously recorded observation that the osmotic pressure of dissolved bodies is frequently—and especially in the case of aqueous solutions—greater than would result from the molecular weight calculated from the chemical formula, thus proving that a partial, and more or less complete, dissociation

of the dissolved substance actually occurs in such solutions. Moreover, it is found that just those substances, and those only, that are capable of conducting the electric current in their aqueous solutions, stand under higher osmotic pressure than is furnished by calculation from the molecular weight in the gaseous condition; that the electrolytic conductivity increases with the degree of dissociation calculated from the osmotic pressure; and that the substances that are good conductors when in a state of aqueous solution, suffer a diminution of this property with the disappearance of the abnormal osmotic pressure when they are dissolved in other solvents.

According, therefore, to our hypothesis, an aqueous solution of hydrochloric acid is decomposed in conformity with the equation $HCl = \overset{+}{H} + \overset{-}{Cl}$, and an aqueous solution of sodium sulphate as follows—$Na_2SO_4 = \overset{+}{Na} + \overset{+}{Na} + \overset{-}{SO_4}$.

Helmholtz assumes the existence of two elementary electrical particles $\oplus$ and $\ominus$ (positive and negative electrons), of which those of like character repel each other, whilst those of unlike character attract one another. According to this view, we should have to regard the free ions as electron compounds. In the first case we should then have—

$$H\oplus + Cl\ominus,$$

but in the second case—

$$Na\oplus + Na\oplus + SO_4\begin{matrix}\diagup\ominus\\ \diagdown\ominus\end{matrix}$$

The case is entirely different with metals, the electrical conductivity of these being generally far superior to that of the best conducting electrolytes at the ordinary temperature; in fact it would appear from recent researches that metallic conduction may attain really enormous proportions in the vicinity of absolute zero (where electrolytic conductivity is imperceptibly minute), whereas at higher temperatures (at

which electrolytic conduction is excellent) that of metals gradually diminishes. Moreover, as already stated, there exists between the two the cardinal difference that the conductivity of electrolytes rests on the conveyance of matter, which cannot be detected in the case of metals.

The tendency at present is to favour the view that metals contain electrical particles which (in contrast to the ions) are devoid of mass, and the migration of which effects the conduction of the electric current. The excellent conductivity exhibited by many metals leads to the assumption that these contain a very large number of such particles, an opinion supported by the fact that matter in the metallic condition is of high density, *i.e.* that the presence of numerous electrical particles produces considerable electrostriction. Under the hypothesis of electrical atoms devoid of mass, we should then have to regard the metals as solutions of electrical matter (ether ?), in which the dissociation $\oplus\ominus = \oplus + \ominus$ has assumed considerable dimensions. A support of this view could probably be found in the extraordinary conductivity of the metals, this being analogous to the increased conductivity of the gases in a state of dissociation.

According to C. Liebenow,[1] the electric conductivity of alloys promises to furnish valuable information as to their constitution. The foundations of his theory are as follows :—

The conductivity of an alloy, calculated from the proportion and conductivity of its components, is generally greater than that actually observed, because of the thermo-electric counter currents set up by the electric current between the various constituents of the alloy.

For the sake of simplicity we may imagine the alloys as composed of alternate superposed plates of the components. If this mass be then traversed by an electric current, the

[1] *Zeits. f. Elektro-Chemie*, 1897, vol. iv. p. 201 ; published in a separate form as *Der elektrische Widerstand der Metalle*, Halle, 1898.

surfaces of contact will exhibit Peltier effects, *i.e.* will be alternately heated or cooled, the alloy in such event representing a thermopile, the electromotive force of which acts in opposition to the current. Moreover, it is clear that this counter current must be proportional to the strength of the current, so that the alloy appears to exert an increased resistance.

Hence the specific conductivity of a metallic alloy can be expressed by—

$$C_0 (1 + \gamma t) = A_0 (1 + at)\ B_0 (1 + \beta t),$$

wherein A_0 represents the actual resistance at zero C. (calculated according to the law of mixtures), B_0 the thermo-electric counter energy, and C_0 the resistance actually observed. a, β, and γ are coefficients of temperature.

Now the coefficient for most of the pure metals is 0·004 (approximately the same as the coefficient of expansion of gases, 0·003663), *i.e.* the resistance of most pure metals increases in proportion to the absolute temperature. On the other hand, the opposing thermo-electric energy alters but very slightly with the temperature, so that the value 0 may be substituted for β.

From the above, Liebenow draws the following conclusions :—

1. As a rule, provided B_0 possesses any considerable value, the specific resistance of an alloy will be greater than that calculated from the components ; on the contrary, the coefficient of temperature will be much less than that of the pure metals.

2. On the other hand, in metals that are thermo-electrically indifferent B_0 is small, and in this case the specific resistance can be calculated from the components ; the coefficient of temperature of such alloys is just as great as that of the pure metals.

3. If the mixing of the metals result in the formation of

a compound, and if the proportions of the components be selected so as to correspond with the composition of that compound, then B_0 necessarily disappears, and the coefficient of temperature becomes equal to that of the pure metals. The presence of an excess of either of the components would cause B_0 to assume an appreciable value, which must be attended by a reduction in the coefficients of temperature.

The resistance curves of metallic alloys (referred to the resistances as ordinates and the volume-percentage composition of the alloys as abscissæ) are parabolic, the axes running parallel to the ordinates; consequently the resistance increases from the pure metals up to the point of equal volume-percentage, whilst the coefficients of temperature follow the opposite course.

From the remarkably low coefficients of temperature of liquid mercury, Liebenow (*Zeits. f. Elektro-Chem.*, 1898, vol. iv. p. 515) drew the highly interesting conclusion that the metal in this condition constitutes an alloy of the monatomic molecules of mercury vapour and the polyatomic solid metal. This assumption finds important support in the fact, discovered by W. von Siemens, that small metallic additions (less than 1 per cent.) to mercury increase its conductivity, whilst larger additions have the reverse effect; also in the relation between the coefficients of temperature and the resistances of solid and liquid mercury; in the diminution of the coefficient of liquid mercury as the temperature is reduced; and by the possibility, discovered by Grunmach, of obtaining solid mercury with higher resistance and smaller coefficients of temperature than it exhibits under ordinary conditions.

A close connection exists between the conductivity and the opacity of metals. On this point Nernst states: "We are unacquainted with any non-metallic bodies that require to be reduced to such thin layers as is the case with metals, before

ɔming transparent. From the standpoint of the electro-
ɲnetic theory of light the optical opacity of the metallic
lition must be ascribed to the circumstances that—in
ɔrast to electrolytic conductivity, where the connection of
tricity is inseparable from that of matter, and therefore
ɜesses appreciable inertia—the metals also behave as good
luctors of electrical vibrations of the high velocity ex-
ted by light waves."

CHAPTER XI

THERMAL EXPANSION

It has been found by H. Le Chatelier (*Bull. Soc. d'Encour.*, 1895, p. 569) that the maxima of the fusing-point curves of metallic alloys do not invariably correspond with that composition of the alloys which would coincide with the definite chemical compound to which the maxima in question are ascribed. Van der Waal (*Archives des Sciences nederlandaises*, 1899), who confirms this observation, proceeds from the law of phases established by Gibbs, according to which the composition of the liquid portion of the solution must be equal to that of the deposited solid body, up to the maximum of the fusing-point curve. The contradiction between theory and experience also disappears immediately when it is assumed that—starting from the definite chemical compound—the composition of the deposited solid continually changes in accordance with the composition of the solution, *i.e.* that the deposited solid body behaves as an isomorphous mixture, or, in other words, that the deposition is that of a solid solution.

In such cases it is necessary, in order to obtain more complete information on the constitution of alloys, to have recourse to other observations in addition to the determination of the fusing-point curves or the points of recalescence; and for this purpose Le Chatelier (*Comptes Rendus*, 12th June 1899; *The Metallographist*, 1899, ii. p. 334) recommends, in addition to the examination of the microstructure,

the measurement of the electrical conductivity and the thermal expansion.

The value of the first-named determination in ascertaining the constitution of alloys has been discussed in the preceding chapter; the measurement of the thermal expansion, however, gives the following indications :—

If an alloy be formed of the alternate juxtaposition of two kinds of definite compounds, or, for example, of one such compound and a pure metal, then the expansion must necessarily remain within the limits of the expansion of the components; if, on the other hand, the alloy exhibit an expansion deviating therefrom in any considerable degree, a solid solution is present.

Le Chatelier selected for his experiments the alloys of copper with antimony or aluminium, because these exhibit very decidedly the above-mentioned anomalies of the fusing-point curves. The results of these experiments are given below, it being premised that the composition of the alloys is expressed in equivalents of copper per 100 equivalents of the mixture :—

COPPER-ANTIMONY ALLOYS.

Percentage Equivalents of Copper.	100	95	90	85	80	57	33	10	0
$10^6 \times$ Expansion @ 63° C.	16·3	19·2	20·2	20	19·2	14·5	11·5	9·1	10

The expansion of the alloys rich in antimony is uncertain, because the expansion of antimony crystals is very unequal in different directions.

COPPER-ALUMINIUM ALLOYS.

Percentage Equivalents of Copper.	100	91	75	60	50	33	30	10	0
$10^6 \times$ Expansion @ 63° C.	16·4	16·3	16·5	15·7	15·8	16·2	20	21·9	24·6

The definite compounds in these two series have the following atomic composition :—

Copper-Antimony Alloys.

Cu 80 per cent. . . . . $SbCu_2$.

Copper-Aluminium Alloys.

Cu 75 per cent. . . . . $AlCu_3$.
Cu 33 „ . . . . . Al_2Cu.

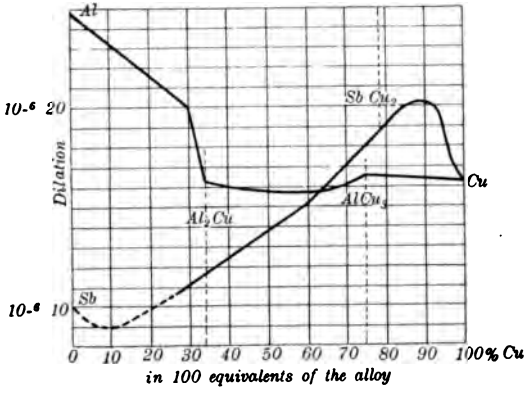


FIG. 29.

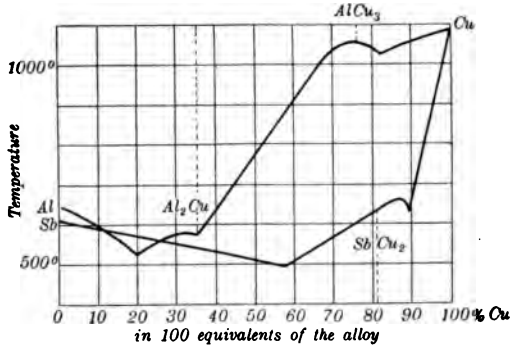


FIG. 30.

The foregoing results are displayed by the graphical method in Fig. 29, whilst Fig. 30 represents the fusing-point

curves of these alloys. A comparison of the two figures shows that the fusing-point maximum of the copper-antimony alloys corresponds to a maximum expansion considerably in excess of pure copper, or of the compound $SbCu_2$. Consequently the alloy corresponding to both these maxima cannot be constructed of alternate crystals of Cu and $SbCu_2$, but must represent a solid solution.

In the copper-aluminium alloys, the compound $AlCu_3$ corresponds to a maximum of the fusing-point curve, and of the curve of expansion, and therefore exhibits no anomalies. On the other hand, the compound Al_2Cu (33 per cent. Cu) does not coincide with a maximum in either curve. The nearest maximum in the fusing-point curves corresponds to the alloy with 30 per cent. of Cu, and the curve of expansion exhibits between 33 and 30 per cent. of Cu a steep ascent which also points to the existence of a solid solution in this case.

If these deductions be correct, the microstructural examination and the determination of the electrical conductivity must also lead to the same results. No results on this point are available in the case of the copper-aluminium alloys; but for the copper-antimony alloys, Kamensky [1] found a maximum of electrical conductivity; and Stead,[2] homogeneous structure; with 80 per cent. of copper, *i.e.* in the alloy that exhibits the highest fusing point and the largest coefficient of expansion.

Other physical properties of the metallic alloys have hitherto scarcely been brought under consideration with a view to the elucidation of their constitution; consequently brief reference thereto will suffice.

The volume of the alloys is in some cases equal to the

[1] *Phil. Mag.*, 1884, vol. xvii. p. 270.

[2] *Journ. Soc. Chem. Indust.*, 31st December 1898; *The Metallographist*, 1899, ii. p. 314.

sum of the volume of their components (gold-copper alloys, antimony-bismuth alloys, etc.), in others smaller (copper-tin, silver-gold), in others again larger (antimony-tin, tin-cadmium, cadmium-lead).

The specific heat of alloys can, according to Regnault,[1] be calculated from that of their components, by the additive method; this, nevertheless, also applies to solid compounds.

The heat of mixture is frequently very considerable, *e.g.* in the case of the conjoint fusion of copper and zinc, the production of sodium amalgam, etc., and in fact sometimes so great as to lead to incandescence.

[1] *Ann. Chim. Phys.*, 1840 (2), 73, p. 5.

BOOK II

MICROGRAPHY

CHAPTER I

GENERAL

THE immediate object of the microscopical examination of metals and alloys is the determination of their microstructure, and to discover the connection between this and the other properties of the metal under examination. It was, however, soon recognised that this microstructure depends not merely on the chemical composition of the alloy, but also on the method of production and treatment; and consequently the aims of micrography were enlarged to include the connection existing between the production, treatment, and structure of alloys within the scope of research. These investigations are of the widest importance, inasmuch as they not only often reveal the way in which the alloy under examination has been prepared and treated, but also frequently afford indications as to the most suitable methods of production or treatment for a particular purpose, and as to how certain defects in the material or method of treatment can be obviated.

Osmond, one of the most noted workers in this branch of science, compares the various tasks of the microscopy of

metals with the different branches of the natural sciences (anatomy, histology, biology, and pathology), and states (*Baumaterialkunde*, ii. p. 63) that the investigation of the metals naturally falls into a number of subdivisions, just as in the case of medical science, so that we can therefore speak of anatomico-histological, biological, and pathological metallography.

The foremost is concerned with the differentiation and determination of the various components of an alloy. This is effected by determining the optical properties, such as colour and lustre, the chemical peculiarities (*e.g.* behaviour towards re-agents, formation of superficial films), and the mechanical properties (*e.g.* resistance to wear and fracture); in addition, an examination is made of their form, whether crystalline or not, their absolute and relative dimensions, the parts exhibiting the minimum of cohesion (surfaces of contact and fissure), either separating the particles from each other, or each for itself.

The second part investigates the modification sustained in point of composition, form, dimensions, and mutual relation, by the different components found in a specimen in normal condition, when subjected to various methods of treatment, whether by mechanical influences or heat, in the course of manufacturing or using the alloy.

Finally, the third part is concerned with the study of defective treatment of the material, and extraneous admixtures, which develop special peculiarities therein. This branch of metallography often enables the reactions elucidated by suitable preliminary investigations to be utilised in solving problems arising in the course of daily practice.

Having spoken of the maladies of metals, it becomes our task to perfect, as completely as possible, the remedies by which these defects may be removed, in order that in this manner the solidity and durability of our edifices may be

ensured. In the attainment of this object, metallography offers a new method of investigation, the appliances of which are daily becoming more perfect and the advantages more apparent.

So far as concerns the microscopical examination of the metals, a complete description of all the methods, instruments, and appliances used for this purpose would exceed the limits of the present work. For our purposes a brief review of them will be sufficient: this is, however, indispensable in order to enable those who have not been personally engaged in similar investigations to suitably appreciate the results obtained.

Fractured surfaces are unsuitable for the purpose of microscopical examination, since on the one hand they only bring into view the parts exhibiting a minimum of cohesion, and on the other hand their irregularity precludes the employment of any but very low powers (ordinary hand magnifiers).

Consequently the examination has to be conducted on cut and polished surfaces, and it is advisable to examine both the surfaces exposed by the cutting. For information as to the various kinds of apparatus used for cutting and polishing, the reader must consult the special literature on the subject.

The simplest method of procedure is as follows:—

Lumps of the metal or alloy, measuring 1–2 cm. in breadth, are separated from large castings, forged, or rolled pieces, by chipping or sawing. These are next filed down into discs, 1–3 mm. thick, with parallel surfaces, which are mounted for polishing by cementing them on to glass, or soldering on to zinc or brass plate. (This latter, however, prevents the formation of superficial colorations.) In the case of hard cast iron, fine crystalline white iron, ferrotungsten, ferrochrome, etc., it is necessary either to break off suitable flat pieces with a hammer, or saw them off by

means of emery and a soft steel disc. In grinding thin plates (0·5 mm. and under) the cementing material is a source of much difficulty, and the following cement will be found to give the best results:—Shellac melted with half its own bulk of soft Canada balsam, the mass rolled into sticks of about ½ cm. diameter whilst still soft, and these used in the same way as sealing wax.

The cut surfaces must then be polished, for which operation no general rules can very well be laid down. Rough grinding is best effected with a hard cast-iron disc, revolving on a vertical axis and strewn with emery powder, the ordinary commercial form being employed at first, and afterwards succeeded by fine, levigated emery. It is necessary to carefully wash the specimen of metal before each change to a finer grade of emery. At the Mechanico-technical Laboratory, Charlottenburg, a machine constructed by R. Fuess of Steglitz, near Berlin, is used for this purpose.

Dry grinding should be avoided, since, in addition to other unpleasant defects, it produces blue colorations on the surface of the metal, and the parts so affected continue to behave in an abnormal manner when etched, even after having been repeatedly cleaned with leather and tin ash.

According to H. Behrens, the fine grinding is effected on fine ground glass with the finest emery, the latter having been previously ground in a little water with a glass or porcelain muller until no further noise is audible.

Polishing is performed with the finest rouge or tin oxide (both strongly calcined and ground till noiseless), mixed with water, two methods being employed.

Ordinary flat polishing is effected on a disc of plate-glass or agate, a high lustre being best obtained by dry polishing on glass or agate. In this event the hardest parts of the structure are revealed by their brighter sheen.

The second method is that of polishing in relief. It con-

sists in completing the operation on a soft pliant backing, so that the different components will be removed to a different extent, and the hardest will stand up in relief. If the constituents differ considerably in their degree of hardness, the structure will be detected under the microscope, without any further treatment being required. This method forms a useful means of determining the relative hardness of the constituents. A suitable backing for relief-polishing is afforded by a block of soft wood, over which is stretched a piece of wetted parchment. A small quantity of jewellers' rouge is used for the polishing. A third method of polishing by etching is described below.

In order to bring up the relief in a particularly decided manner, H. Behrens grinds the specimen with emery and water on a ground glass plate until a fine matte surface has been produced, and then, after rinsing, polishes for a short time with tin ash and a very little water, on wood. By the action of the granular grinding materials, the softer and more crumbling particles are most attacked, and the brief polishing acts merely on the parts in relief, which it brings more prominently into view by their increased lustre.

In flat polished specimens, and also in those polished in relief, when the differences in the hardness of the constituents are not sufficiently accentuated, difficulty is experienced in differentiating the components under the microscope unless they are differently coloured. To render them more clearly apparent, the polished surface is subjected to certain chemical and physical treatments, which differ with the nature of the materials. The chief among these processes are etching and coloration.

Wedding advises that, previous to etching, the polished surface of metal should be brushed over whilst immersed in chloroform, and then cleansed with alcohol and ether. This method, however, suffers from the defect of over-rapid

evaporation, the result of which is that, despite the utmost care, there frequently remain behind on the surface of the metal streaks and rows of grease spots. Moreover, the rapid evaporation of alcohol and ether produces condensation of atmospheric moisture, which, if not evaporated in a uniform manner, may also give rise to disturbances of the experiment. For these reasons both Behrens and Storby accord the preference to rubbing with dry polishing materials, such as tin ash or Viennese lime, distributed on a rag or piece of fine-grained wood. In using rags or pieces of cloth, care is necessary, since fragments of soap may be conveyed to the surface of the metal, and, with the assistance of moisture, produce most surprising streaks and tufts when the specimen is etched and coloured. Even the use of fine leather requires the exercise of care, both chamois and glove leather sometimes containing a large proportion of fat. Nevertheless, it may be very useful after rubbing with tin ash or Viennese lime.

Two purposes are served by etching: either merely the different attackable parts are to be rendered visible, or the individual constituents acquire different colorations. The first eventuality chiefly happens when the constituents are so small as to be undistinguishable, even under the microscope. The irregularities produced in the surface by the action of the etching reagent cause the decomposition of the reflected light; and in proportion as the etching is deeper, yellow, brown, blue, and black shades appear in succession (in normal light), without, however, representing any actual coloration.

The reagents employed for etching frequently consist of very dilute acids. Osmond recommends dilute nitric acid, its action being the more rapid the harder and more impure the metal. Dr. Sorby also etches with very dilute nitric acid (one volume of 56° B. acid and four of water) for a few seconds,

one minute at most. If the etching is insufficiently strong, he dips the specimen in the reagent for another five to ten seconds, and repeats this operation until it is etched enough. After each immersion the specimen must be examined under the microscope. Wedding advises hydrochloric acid (1 : 100), and both this worker and Martens recommend hydrochloric acid diluted with alcohol or ether; however, in the latter event, the ground specimen must be moved up and down on a platinum gauze, the access of air being prevented by an elastic cover attached to the handle of the gauze.

H. Behrens recommends nitric acid of specific gravity 1·3 for preliminary experiments, on account of its clean and rapid action. According to this worker, the relief produced by the Wedding process is so slight that the detection of any structure is difficult, even when the specimen is held in a slanting direction towards the light. In this case the coloration is the principal thing, the etching, which alters the polished surface in accordance with the structure, being only a preparatory process. It is undeniable that very minute details of the structure can be rendered visible in this way; but it must not be forgotten that great care is necessary. It is better to carry the etching somewhat further, effect the two operations side by side, and compare their results. The pictures do not always entirely harmonise, the etching usually giving more detail and sharper outlines.

The etched plates must be immediately washed in a large volume of water, then in alcohol, and dried on filter paper. The best way to complete the drying without risk of oxidation is by means of a current of air discharged under pressure. If, as often happens, the picture be dimmed by a film of carbon produced during etching, it is dried by applying soft linen cloths.

Albert Sauveur adopts the following method of etching: —The specimen, properly ground and fixed in position, is

placed in concentrated nitric acid (sp. gr. 1·42), which, in consequence of the resulting passivity of the iron, exerts little or no action on the polished surface. The specimen is then placed under a strong current of running water, and the acid washed off completely with care. Immediately the layer of concentrated acid in contact with the surface is diluted by the water, it attacks the steel; at first the action is very powerful, but, as the water soon removes all trace of the acid, the reaction lasts such a short time that all risk of over-etching is precluded. This method of treatment develops the etching sharp and clear, and the etching is uniform over the entire surface, without any formation of disturbing coloured films or inequalities in the appearance of different parts of the polished surface, such as produce deceptive results when dilute acid is used. Oftentimes it is necessary to repeat the etching in order to render the development of the structure more clearly defined, but more than a second immersion is seldom required. The specimen is then washed with alcohol, and quickly dried with a soft cloth, or, preferably, in front of the jet of a blower, when the latter is available.

An excellent method of etching with iodine tincture has been given by Osmond,[1] and furnishes very good results. It consists in pouring over the surface of the specimen one or two drops of iodine tincture (one drop per sq. cm.), and leaving the same to act until it loses its colour. The surface is then washed with alcohol, and dried quickly with a soft cloth or in front of a blower. Sauveur prefers iodine tincture diluted with an equal volume of alcohol. Frequently this operation must be performed twice, or even more, in order to obtain a satisfactory etching. This treatment with iodine tincture is particularly advisable when it is desired to bring out the finest details of the structure (as in the case of the

[1] "Méthode générale pour l'analyse micrographique des aciers au carbon," *Bull. Soc. Encouragement*, May 1895.

tender scales of pearlite), whilst for examinations with low powers the nitric acid method is more effective.

Osmond has also given another special method of etching, which consists of a combination of the operations of polishing and etching, the metal being polished with Vienna lime (gypsum) and liquorice extract, on a backing of parchment. F. Osmond and G. Cartaud [1] recently recommended, for etch polishing, the use of a solution of two parts of crystallised ammonium nitrate in 100 parts of water. The parchment, stretched over a block of wood, is soaked with this solution, and the polished surface of the specimen is ground therewith until sufficiently etched. Should the parchment become dry, it may be moistened with a little water. The effect is just the same as that of liquorice extract.

As we shall see later on, the typical structure and the nature of the micrographic constituents of steel vary with the temperature. It therefore seemed of interest to also perform the etching process at higher temperatures, for which purpose Saniter employs fused calcium chloride as the etching fluid.

A second method for rendering the several constituents of a metal clearly visible consists in producing on the surface of the metal a firmly adherent patina, which, though too thin to possess any colour of its own, nevertheless exhibits, by reflected light, colorations that vary according to the thickness of the layer. As these colorations do not show up at all on non-oxidisable metals, and not concurrently on metals of different degrees of oxidisability, this method of investigation is frequently employed. It furnished Martens with the beautiful figures on spiegeleisen that illustrate his first report [2] and form one of the first successes of metallography.

The metal in question consisted of two components, a carbide of the definite composition $(FeMn)_3C$, and a solution of carbon

[1] *The Metallographist*, iii. pp. 1–3.
[2] *Zeits. Vereins deutscher Ingen.*, 1878, Plates 24 and 25.

(or carbide) in the remainder of the alloy. The oxidisability of the carbide is relatively small, and exposure to a certain temperature for a given time produces, for example, a yellow coloration, whereas the remainder of the alloy has already attained the blue condition. The colour shades obtained in this way have the great advantage of not disappearing under a high magnifying power. Considerable use has been made of these colorations, which are specially valuable in the investigation of alloys of copper, by Wedding,[1] Behrens,[2] and Guillemin.[3]

Wedding states that the colorations should not be pushed beyond the brown yellow of the first series.[4]

[1] *Journ. Iron and Steel Inst.*, 1885, p. 187.

[2] *Mikroskopisches Gefüge der Metalle und Legierungen.*

[3] *Commission des méthodes d'essai des matériaux de construction*, I. Serie; Rapports, vol. ii. p. 19.

[4] The serial order of these colorations—arranged in order of increasing thickness—is as follows:—

Series.	Colour in Reflected Light.
I.	Black. Dark lavender grey. Pale lavender grey. Very pale lavender grey. Bluish white. Greenish white. Yellowish white. Pale straw yellow. Brownish yellow. Orange. Red.
II.	Purple. Violet. Indigo. Sky blue. Pale sky blue. Very pale bluish green. Pale green. Yellow green. Yellow. Pale orange. Red.
III.	Purple. Violet. Blue. Sea green. Green. Pale yellow green. Fawn yellow. Red.
IV.	Purple, then dull purple. Greyish blue. Sea green. Green and greyish green. Greyish red, red, dull red.
V.	Bluish green, dull initially and finally. Flesh tint, dull initially and finally.
VI.	Bluish green, initially dull.

This is correct for iron poor in carbon; but, according to Behrens, one may go further in the case of white iron, and still further in the case of ferrochrome, for which last reddish violet of the second series is preferable. In iron and steel there are also basic salts that come into play, the formation of which is difficult to avoid when very dilute acids are used. They colour rapidly, but comparatively dull. The worst case that can happen is when a film of this kind becomes broken into a fine network in drying, which network afterwards shows up with remarkable contrasts of colour. Air-bubble pittings, enclosed particles of slag, and imperfectly closed weldings, stubbornly retain small quantities of iron salts, which come out on to the surface in drying, and give rise, during the coloration, to highly complex figures, which can the more readily be referred to peculiarities of structure, inasmuch as they appear in the vicinity of defective places.

Annealing pushed very far may have the effect of an etching. If steel be heated to incipient redness, and then quenched in water, there will appear, in the places where the oxide skin has become detached, figures closely resembling those produced by etching. These "fire figures" are almost always to be found on hardened steel, being shown up by fine grinding and polishing, and are attributed to differences of hardness, which, however, seems at anyrate doubtful from what has been stated above.

Another means of differentiating and characterising the various micrographical constituents is afforded by the determination of the degree of hardness. A preliminary estimate of this quality can be formed from relief grinding: for more precise testing, Behrens employs sharp-pointed needles of different degrees of hardness, which are stuck into the specimen and pushed forwards like a graver. If the needle be softer than the specimen under examination, it slips over

the surface, and the point is duller and turned on the application of greater force; whereas, if the needle be harder than the specimen, it ploughs its way through the metal. For this purpose Behrens makes use, *inter alia*, of the following materials, the hardness of which, on Moh's scale, is appended to each:—Lead, H = 1; tin, H = 1·7; ferruginous tin, H = 2; hard lead, H = 1·5–2·2; zinc, H = 2·5; copper, H = 3; brass wire, H = 3·1; gunmetal, H = 3·3; bronze with 12 per cent. of tin, H = 3·5; bronze, with 18 per cent. of tin, H = 3·7; iron wire, H = 3·7–3·9; sewing needles, H = 5–5·5; similar needles heated till coloured yellow in the third series, H = 4; if heated to blue of the second series, H = 5; steel for metal drills heated to yellow of the second series, H = 6; chrome steel, H = 6·2–6·5; ferrochrome, 50 per cent., H = 7–7·3. In the case of bronzes, Martens succeeded in measuring the hardness of the various portions of the structure by means of the sclerometer.

Resistance to scratching chiefly depends, as Osmond observes, not only on the nature of the substance, but also on its absolute dimensions. A glass plate, when sufficiently thin, can be cut with the finger nail, even if not scratched thereby.

For testing the weakest place of a ground microscopical preparation, Stead proposes to subject it to flexion, either by continued pressure or by a blow. The simplest way to perform this test is to lay the specimen, polished side downwards, on a block of steel, provided with V-shaped grooves, over which latter some force is applied to the preparation. Should the piece sustain fracture, which is frequently the case, this does not prevent the examination of the weakest portion under the microscope. All that is necessary is to place the two broken pieces side by side on a glass slide, and bring the latter under the instrument. The value of this method can be seen from Figs. 31 and 32, Plate III.

Fig. 31 shows a piece of wrought iron which was bent in a direction parallel to that of the rolling, and demonstrates that the weakest place coincides with the position of enclosed particles of slag. Fig. 32, on the other hand, shows that the line of fracture in cement steel runs parallel to the deposition of iron carbide.

Further assistance of an important character is afforded, in the microscopical examination of polished sections of metal, by chemical analysis, of which only one branch need be mentioned here, namely, the method of fractional analysis employed with great advantage by Behrens. This is suitable for application in all cases where a relief exceeding 0·1 mm. in depth can be produced; and is of particular importance in connection with the alloys of iron, where the form, coloration, differences of hardness, and behaviour towards solvents, prove insufficient to detect the numerous admixtures with accuracy.

According to Behrens, the ground sections subjected to fractional analysis must be perfectly even, though careful fine grinding and polishing are unnecessary.

In the case of white iron, ferromanganese, ferrotungsten, etc., the etching is commenced with strong hydrochloric acid containing an admixture of about 5 per cent. of nitric acid. When an evolution of hydrogen occurs, the etching liquid is removed by means of a glass tube, drawn out in the form of a pipette, and is heated in a basin or porcelain crucible with a little nitric acid until oxidation is complete, after which it is applied again, a little hydrochloric acid being added if necessary. This treatment having been repeated two or three times, the solution is set aside in a capillary tube for examination later on, the metal is rinsed, wiped with a filter paper followed by a clean rag, and examined under a low power (30- to 40-fold magn.). If the projecting portions are bright, the surface is treated with hydrochloric acid containing 8 to 10 per cent.

of nitric acid, the same procedure being adopted as in the first etching; and the treatment is continued until these portions are attacked, the last solution being then discarded. White iron will stand two etchings, sometimes three, the operation taking about an hour. Ferrochrome will stand more than 20 per cent. of nitric acid, and can be etched to a depth of 1·5 mm.

The next task is to obtain reliable samples of the projecting parts of the etched section, which is accomplished by attrition on perfectly even, dull-ground surfaces, agate being used in the case of hard iron alloys. The etched section is cleaned by brushing it under water containing a few drops of acid, followed by water alone, the preparation being then ground—either dry or with a single drop of water—on agate until the latter exhibits a film of metallic powder. This powder is finally rendered accessible to examination (generally microchemical) by the aid of suitable solvents.

So far as microscopical examination is concerned, low powers (50- to 100-fold magn.) are sufficient in many cases, though powers up to 200 or 300 are not infrequently employed; and in some instances, where the elucidation of very fine details is in question, recourse must be had to powers as high as 1000-fold, or even greater. For low powers ordinary daylight will afford sufficient illumination, provided the object be held in a sloping position, unless deeply etched or exhibiting high relief. For higher powers, recourse must be had to special illuminating devices, of which there are several types available.

As regards the choice of a microscope, it is best to select one made by a firm of repute, such as Zeiss of Jena, Reichert of Vienna, and others.

Wedding, Osmond, and Guillemin photograph the microscopical picture, whereas Martens and Behrens prefer to draw it with the aid of a prism.

CHAPTER II

MICROSTRUCTURE

THE microscopical examination of even simple metals exhibits a particular structure instead of a uniform surface (see the example given in Fig. 33 of Plate IV., which represents silver magnified 20 diameters). The metal exhibits a cubical structure, consisting in turn of a number of cubes in regular juxtaposition. This structure owes its origin to the crystallisation that usually starts from the surface of the solidifying metal or the walls of the mould in which it is cast. In this case the first crystals are generally arranged along straight lines, nearly at right angles to the cooling surface, and from these crystals of the first order branch crystals of the second order at right angles thereto.

In some cases, especially copper and the silver alloys rich in copper, crystallisation seems to occur at certain centres within the mass, before beginning at the surface. In such event, the interior of the mass exhibits radial lines of crystals interrupting the regular crystalline structure, and separated therefrom by a confused layer of finely crystalline metal.

The individual morphological elements of the metallic structure are usually termed crystals, though Stead calls them "grains," and definitely distinguishes them from crystals. On this point he expresses himself as follows:[1]—

Grains and crystals must not be confounded together, though the former are built up of the latter. The grains

[1] *Journ. Iron and Steel Inst.*, 1898, i. p. 183.

resulting from the solidification of liquid metal are large or small, according as the cooling proceeds slowly or quickly; their shape is influenced by the adjoining grains formed at the same time.

Osmond also says of these grains that they are not of true crystalline structure, since they do not exhibit any true contour surfaces, nor are they of any regular geometrical form. They are, however, not homogeneous, since their attrition when polished on parchment is not uniform, nor are they uniformly attacked by etching reagents. The cause of this difference resides, partially at least, in the crystalline arrangement of the structure, which changes from grain to grain though remaining uniform throughout the full extent of one and the same grain, as a deeper etching will reveal. Thus, if we have a metal crystallised in cubes, it will be found that the grains which are cut in a direction parallel to two axes will exhibit small regularly stratified cubes, whereas the grains in which the cut runs parallel to a single axis will have a flaky structure, and those that have been cut parallel to no axis at all will reveal merely an indefinite structure.

Consequently we have a double system of surfaces of minimum cohesion. The one is due to the shaly structure of the interior of the grains; the other to the mutual limitations of differently oriented, superimposed grains. The structure of the metals is therefore dependent on the extent to which the individual crystals are restricted or not during their development. In the former event the metal will consist of grains, in the latter of crystals, and a distinction may therefore be drawn between different species of structure.

According to H. Behrens, cast metals frequently exhibit a reticulated or a scaly structure, these modifications resulting from the juxtaposition of fairly similar octahedra, cubes, and cuboid rhombohedra. In places the uniform texture is interrupted by radio-sphærolithic concretions.

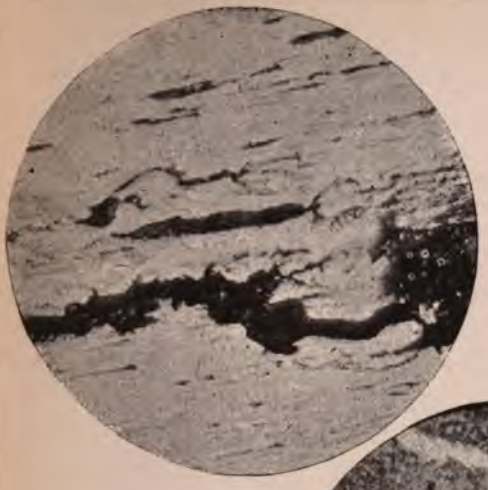


Fig. 31.
Wrought iron
with
embeddod slag.

Fig. 32.
Iron carbide
in
cement steel.

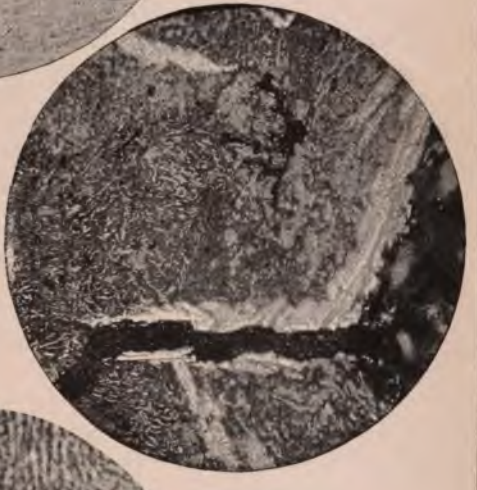


Fig. 34.
28% Cu, 72% Ag
cast and
exposed
until
purple red.
Magn. 1000 linear.

Specially printed for Scott, Greenwood & Co.

THIS
PUBLIC

By rolling, the reticulated structure is first changed into the form of scales, and afterwards, by extension in two directions, into shaly structure. Etched sections exhibit zigzag lines in the former case and wavy lines in the latter. Drawing produces fibrous structure, indicated by fine parallel lines disappearing at intervals. If the metal have been extended partly by forging and partly by rolling or drawing, a wavy-fibrous structure will be developed. Forging, without any other treatment, may lead to a confused fibrous, felted structure. The protracted working of metal free from slag, whether by rolling or hammering, accompanied by frequent re-heating, will finally give a fine-grained structure, without any definite contours of the crystals or predominant direction of the sutures.

The influence of temperature on the structure produced by working the metal will be dealt with later on.

If the metal be impure, the intimate juxtaposition of its crystals may be hindered by included matters. Oxides and sulphides may be dissolved by the liquid metal at high temperatures, and then suffer deposition during the process of crystallisation. This deposition occurs, either in the form of small diffused particles disseminated throughout the mass of microscopic crystals, in which event inclusions are formed within the finished groups of crystals; or in the form of films or thin plates on the boundary surfaces of large crystals or crystalline aggregations. Thus, according to Behrens, cuprous oxide is found deposited in copper, oftentimes in far from insignificant quantities; and occasionally silver sulphide in silver, without being visible on polished or on cast surfaces, though revealed, as fine brown lines, arranged in regular order, on etched surfaces. A similar behaviour may also be exhibited by metallic alloys. In the case of an alloy of 80 per cent. copper and 20 per cent. lead, an almost entirely lead-free copper will crystallise out, and lead containing only a very

small proportion of copper will be found, in an almost amorphous state, deposited between the crystals; the same thing occurs with zinc and lead. On the other hand, a different behaviour is noticeable in alloys composed of copper and tin, or copper and zinc. Here the copper retains a considerable quantity of the more fusible metal, and forms therewith well-developed yellow crystals, between which is found a badly crystallised, or apparently amorphous, alloy, containing a far higher proportion of tin or zinc. This behaviour is analogous to that of water in presence of salts capable of absorbing water of crystallisation. Thus a hot solution of sodium sulphate will deposit, during cooling, crystals of the composition $Na_2SO_4 + 10H_2O$ (*i.e.* with 48·2 per cent. of sodium sulphate and 55·8 per cent. of water), leaving behind between the crystals a liquid which, at 18° C., consists of 22 per cent. of sodium sulphate and 78 per cent. of water.

The well-developed crystals represent the deposited matters, the badly developed crystalline maze, the mother liquor or the eutectic mixture. Moreover, eutectic mixtures are frequently characterised by a foliated structure, in that they consist of alternated flakes of the two components of the solution (see Fig. 34, Plate III., which represents an alloy of 72 per cent. silver and 28 per cent. copper).

The foregoing explains the divergent structure of alloys. Among this class of bodies the reticulated structure is of frequent occurrence, the sparingly represented intermediate matter appearing in the form of threads of a loose irregular net. As the amount of intermediate substance increases, the edges assume a washed-out appearance, the parts they surround being rounded off; paving-stone structure (white iron). If this be very fine in grain, we have granular structure (grey iron). Concretionary structure is also frequent; radial agglomerations, also regular growths of microliths in a micro-crystalline, more or less granular matrix.

When this structure is further developed we have a microlithic felt (radial white iron). Stalky and fibrous structure may be mentioned as special peculiarities of certain alloys, and indicates prismatic crystals belonging to the rhombic or monoclinic system. It may occur with dendritic branchings in an abundant, granular-crystalline intermediate mass (crude cement steel, 20 per cent. ferrochrome), or without branching, the intermediate substance being sparse (high grade ferrochrome, ferromanganese, and ferro-aluminium).

255391

CHAPTER III

THE MICROGRAPHIC CONSTITUENTS OF IRON

As we have seen, the alloys in general are not homogeneous substances, but for the most part constitute a mixture of various microscopic constituents. Of course this applies equally to the alloys of iron.

If, at first, we leave all extraneous admixtures out of consideration and merely take the pure iron and carbon, the following formations can be distinguished under the microscope:—

(a) Cavities—

(a) with smooth surface, and containing hydrogen and carbon non-oxide . . . Gas bubbles.

(β) with rough surface, and either empty or filled with air . . . . . Irregular cavities.

(b) Slag inclusions.

(c) Graphite (and tempering carbon).

(d) Ferrite.

(e) Cementite.

(f) Martensite.

(g) Austenite.

(h) Pearlite.

(i) Sorbite.

(k) Troostite.

($a\,a$) *Bubbles.*—The literature on the formation of bubbles is fairly copious. The most important paper, for the purpose

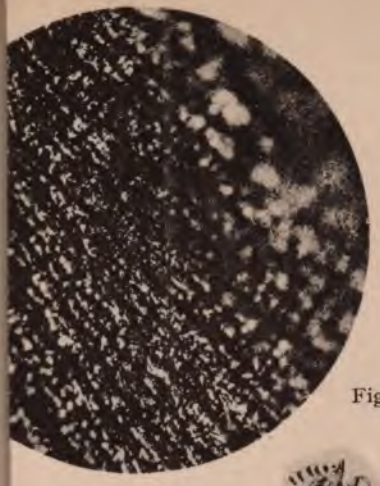


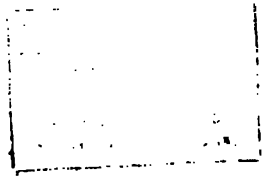
Fig. 37.

Fig. 40.

Fig. 42.

Fig. 43.

Specially printed for
Scott, Greenwood & Co.



ow in view, was compiled by Martens,[1] and from this the rawings now reproduced have been taken.

The chief peculiarities of these bubbles, their pear-like to ermiform shape, flat base, step-like structure, situation in the lock, and the direction of their principal axes, are readily isible in Fig 35, Plate IV. The large bubble in the centre is hown on a more highly magnified scale in Fig. 36, Plate IV., or the purpose of better indicating the striation at the bottom. The bottom of a bubble in a block (pig) of ingot iron is repre-ented in Fig. 37, Plate IV., magnified 10-fold. This reveals he furrows on the walls, and shows them to be interspersed with numerous knobs and protuberances, the form of which becomes more clearly defined when higher powers are used.

The origin of bubbles may be imagined as occurring in the llowing manner:—In any event the steel must, at the time e bubbles are formed, be in such a pasty or viscid condition to preclude their escape to the surface. It may be assumed at the bubbles must undergo shrinkage when the block ols down further in the viscid and still plastic condition, d the bubble receives no further supply of gas. It is not possible that the furrows in the bubble result from such traction, and represent the folding on the surface of the bble. Up to a certain time, adjacent bubbles will be able draw closer together, those moving the more easily attach-themselves to the more sluggish ones—which explains the ward growth of the bubbles situated near the edge, also eir step-like structure, their vermiform shape; which latter often changed into that of a pear with its flattened base wards the centre of the block, when the cooling and forma-n of bubbles proceed at a rapid rate. The bottom remains stic longer than the rest, and is pressed inwards, in con-quence of diminished gas pressure, when the bubble shrinks.

The foregoing sketch illustrates the broad lines of the

[1] *Stahl und Eisen*, 1887, No. 4.

process, but there are smaller details, which can also be traced from the microscopical examination of the finished bubble. Thus the supply of gases, in the form of very small bubbles, has undoubtedly continued up to the very last,[1] since the surface of the bubble walls and the aforesaid protuberances is generally found to be covered with innumerable dotted granules and pittings, which, under favourable circumstances, good illumination, and high powers, are revealed as globular bodies, interspersed with pitted depressions, and as depressions with a central protuberance. The pits are often surrounded by a swollen annular rim. In fact we are here in presence of phenomena often found on a larger scale in the crystal cavities of spiegeleisen (Fig. 38, Plate IV.). An examination of the details shown in Fig. 38 will make it clear that the formation of bubbles is there in question, some of them still in a perfect condition, whilst others have suffered rupture and subsidence just before the solidification of the mass. The latter are undoubtedly older in formation than the former. Whilst some of the rounded protuberances are due to the formation of bubbles, they may also owe their origin to another cause, as we shall very soon see. The occurrence of bubble formation can only be regarded as proved when at least two of the above-mentioned stages, in point of age, are discovered existing side by side, which is usually not a difficult task.

However, the origin of the other multifarious formations at the bottom of these bubbles cannot be ascribed to the production of the bubbles themselves, except in a minor degree. True, a small bubble bursting with some force into the larger space at the last moment may throw up thickened edges or project the substance of the wall, which then solidifies in the peculiar shape thus produced; but the greater probability is

[1] Dr. F. C. G. Müller, "Untersuchungen über den Gasgehalt von Eisen und Stahl" (*Stahl und Eisen*, 1883, 1884).

that the adjacent particles which give rise to the structure of the steel solidify at different rates in the cooling process, that slight alterations in volume on the part of these various alloys in cooling set up tensions, which finally press the still plastic parts of the mass, in the form of rays of a greater or smaller degree of fineness, between the already solidified portions of the walls of the bubble. In the course of their exudation the plastic masses undergo all manner of distortions and modifications, as may be shown with plastic clay forced through a sieve containing openings of different shapes. That the exuding mass still retains a certain capacity—perhaps due to the pressure of imprisoned gases—to distend, or contract into a rounded form, and even to crystallise, can be readily admitted, in view of the divers shapes assumed, which vary from excrescences of the fineness of a hair (sometimes swelling up into decidedly globular masses in places) to indubitable depositions of dendritic crystals (pine-tree crystals). These deposited crystalline aggregations, however, are less frequently found within the cavity of the bubble than on the surface of the walls.

The formation of bubbles of the kind mentioned above has also been regarded as a proof that here occur, on the crystal surfaces of scorched steel (Fig 39, Plate IV.), processes that are attended with liberations of gas within the mass: this question, however, requires thorough investigation.

($\alpha\beta$) The second class of cavities is produced through the contraction of the mass during solidification and cooling, the influence of which is naturally most apparent in the places where the metal remained longest fluid. They are recognisable by their rough surface. The dimensions of these cavities increase with the contraction of the metal, the difference between the casting temperature and fusing point, and with the volume of the casting.

The interior of these cavities may naturally exhibit a very

similar state of things to that prevailing inside the gas bubbles; most frequently, however, they are found to contain crystalline formations like those shown in Fig. 40, Plate IV. The octahedral form of crystal will be clearly recognised. Of course in rolled steel it is impossible to detect even residual traces of the same. These dendritic crystals, as shown in Fig. 40, Plate IV., often attain considerable size; the one illustrated in the figure was found in a cavity in an ingot of mild Martin steel.

Sometimes the apices of the crystals have undergone modification into a globular form that might easily be confounded with the hemispherical bubbles already mentioned, though really of a different nature (Fig. 42, Plate IV.). Their true character can only be determined by the aid of good sections of these globules, sufficiently large specimens of which, however, are obtainable only with difficulty.

A noteworthy and somewhat rare occurrence of crystals has been described by H. Martens[1] (Fig. 43, Plate IV.). The diameter, however, was only 0·02 mm., and therefore the chemical composition could not be determined.

(*b*) *Slag.*—What are generally spoken of as slag inclusions may be of highly divergent nature. Apart from accidental inclusions, such as particles from the material of the mould, etc., there may also be present, in addition to actual slag inclusions, depositions of oxides and sulphides (principally FeO, MnO, FeS, and MnS).

According to Osmond, Fig. 44, Plate IV. represents a slag inclusion in simply polished steel. According to Arnold, similar inclusions may also consist of iron sulphide. The occurrence of oxides and sulphides was mentioned in the preceding chapter.

Mention is here necessary that great care must be exer-

[1] *Zeits. d. Ver. deutscher Ingen.*, xii.

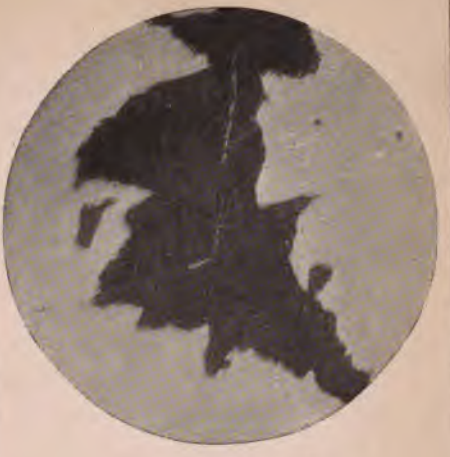


Fig. 44.
Slag embedded in steel.
Smooth polished.
Magn. 1000 linear.

Fig. 41. $^1/_2$ nat. size.

Fig. 45.
Grey pig iron.

cised in pronouncing an opinion on cavities. First as regards their shape, it may, for example, happen that a slag inclusion intersected in a direction transverse to its longitudinal extension, exhibits rounded structures similar to bubble cavities. A. Martens, who has thoroughly described these phenomena,[1] says of them: Cavities of this kind may also be formed as the result of etching an easily corroded substance, as well as produced by artificial means. The former eventuality may arise, for instance, when Thomas slag has been rolled out into veins, which, being filled with resistant material, more or less retain their original section; when etched, the contents are quickly corroded, and a depression (pore) is the result. The second case may occur when a hole, punched out as it were by the grinding material, is not at once eradicated in polishing, and especially when a grain is subsequently deposited and rolled about in the said hole for some time. This may produce a circular depression, with flat bottom and nearly vertical side walls, which, under superficial observation, may be taken for a "pore."

There are also cavities that have been produced owing to the dropping out of originally present structural components (*e.g.* fragments of graphite) during the operations of grinding and polishing; the nature of these, however, can generally be easily recognised from their characteristic form.

(*c*) *Graphite* reveals itself in the form of dark flakes, which appear in section as straight or crooked lines. These flakes often fall out during grinding, in which event so-called "graphite cracks" are found during the microscopic examination (Fig. 45, Plate V.). Graphite flakes may attain a length and breadth of several millimetres, with a thickness of 50-100 μ. More rarely pulverulent graphite is met with, and even this may consist of very minute flakes.

According to Martens, Figs. 46 and 47, Plate VI. show

[1] *Stahl und Eisen*, 1892, No. 9.

the appearance of graphite flakes as exhibited on the surface of grey pig iron.

On polished surfaces graphite is chiefly found in cross-section through the flakes. In the case of large flakes these sections are mostly crooked. In grinding, it frequently happens that the graphite flakes are rubbed out, leaving only the fissures ("graphite cracks") behind.

Behrens has described the following peculiar phenomena, and referred them to depositions of graphite. The ground surface of grey iron occasionally exhibits thin flakes as sharp, lustrous projecting ribs, as well as lustrous dots of similar appearance. Both these are very frequently seen on etched sections (Fig. 48, Plate VI.), where the ribs and dots stand out from a dull ground of grooves and pits. The first inclination is to think of admixtures of hard ferrosilicon or iron phosphide, and to ascribe thereto the projection and glitter of these objects. Lowmoor grey iron may be cited as a good example of large projecting flakes; and accumulations of graphite scales are also frequently met with in fine-grained cupola iron. On etched sections they appear as warts, lying in small shallow pits; and on polished sections they may also take the form of warty projections. Tests for hardness performed under the microscope, however, show that the glittering dots in these accumulations and the protruding ribs on coarse-grained grey iron are far too soft to be ferrosilicon or iron phosphide, the hardness being generally less than 2 and never attaining 4, the hardness of iron itself. Consequently almost the only assumption open is that the low friability of the graphite has enabled it to withstand grinding better than the granular iron.

Tempering carbon (see following Book) affords little variety under the microscope; it is amorphous, whereas graphite, as is well known, crystallises according to the hexagonal system.

(*d*) *Ferrite.*—This substance was named by Howe, and is pure, or nearly pure—at anyrate carbon-free—iron. Relief grinding gives it a dull polish; when subjected to prolonged polishing, especially when finished with gypsum and water, it granulates at a rate and depth inversely proportional to the thickness of the ferrite. When present in larger masses it sets together in the form of polyhedral granules. Each polishing produces the same phenomena more speedily; in this case the ferrite does not assume more than a faint yellowish coloration, if at all.

Etching with iodine solution leads to the same results, and etching with nitric acid also brings the grains up into prominence, either coloured or not, according to circumstances. On this point Osmond gives the following information:—Extra mild steel etched with dilute nitric acid (2 vols. of 36° B. acid and 990 vols. of water) for half an hour exhibits a few grains stained yellow or brown—the coloration probably resulting from a thin layer of oxides or basic salts; others are roughened, whilst others remain unaltered. The brown coating adheres on drying. 2 vols. of nitric acid per 100 vols. of water will produce all imaginable shades in transition, but the coloration is destroyed by wiping. 20 vols. of nitric acid per 100 vols. of water reveal the granular structure, but no coloration remains after wiping.

More particular information about the structure of these ferrite granules has been afforded by the researches of Stead. Thus deeper etching, or the use of special etching reagents, such as copper-ammonium chloride (1 : 12 to 1 : 30), produces on the surface of the ferrite granules uniformly arranged "etched figures" (such as are visible on all crystalline bodies when suitably etched), which, when highly magnified, assume the appearance of imprints made by a minute cube in various positions on a soft substratum. The shape and position of the etched figuring are the same in various parts of the same

granule, *i.e.* on uniformly crystalline surfaces, but differ in adjoining granules. This peculiarity affords a scientific basis for determining the number and dimensions of the individual ferrite granules, even in difficult cases. Low powers of magnification are insufficient to show up the adjacent individual etched figures; on the contrary, the separate ferrite granules appear partly light, partly yellow to dark brown, in colour, and oftentimes even black. The cause of this optical behaviour can be gathered from Fig. 49, Plate VII., which represents various diagrammatic sections of ferrite granules. Each consists of a uniformly stratified aggregation of cubes, the faces of which are inclined at various angles towards the surface of the section. Such of them as are nearly parallel to this surface reflect the rays of light into the tube of the microscope, and therefore appear light in colour; whereas in other instances the rays of light are more or less dispersed, and the ferrite granules then have a correspondingly darker appearance.

Stead found that the presence of phosphorus, aluminium, and especially silicon (in large quantities) produces a very well-defined development of the cubical elementary crystals of these ferrite granules.

A few other observations of this worker, in respect of ferrite granules, may be referred to in this place. He found that, in the case of iron and steel nearly free from carbon, prolonged heating to 600–750° C. (dull red heat) gave rise to an extremely coarse-grained structure, which, however, on the heat being increased to 900° C. and over, passed over into the normal fineness of grain.

This phenomenon does not appear in the case of steel with more than 0·2 per cent. of carbon; so that a wide difference exists between steels respectively rich and poor in carbon.

According to Stead, the crystalline axes of the adjacent granules, which are placed at highly divergent mutual angles,

Fig. 46.

Graphite crystals from Langloan I, obtained by dissolving in HCl.
$^1/_{50}$ n. S.

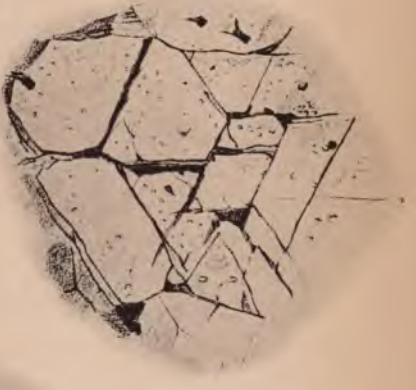


Fig. 47a.

Part of Fig. 46, highly magnified.

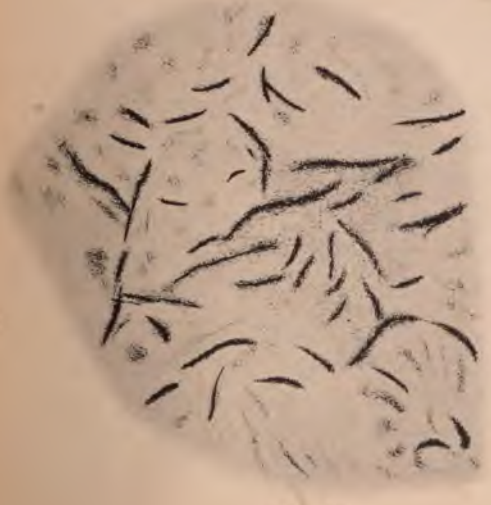


Fig. 48.

Fig. 47b.
$^1/_{250}$ n. S.

Specially
Scott, Gr

change their position, during the interval of temperature in question, until their direction coincides; whilst at the same time the lines of demarcation between the granules disappear, thus giving rise to larger granules.

Thus it follows that, in the case of iron with less than 0·1 per cent. of carbon, prolonged heating at dull redness is inadvisable, though this was formerly regarded as quite innocuous. This behaviour explains the brittleness and coarse fracture sometimes exhibited by very mild steel, and for which chemical analysis has hitherto failed to detect any cause. When the orientation of the individual crystals is throughout the same, or nearly so, a condition the metal tends to attain when subjected to prolonged heating at the temperature in question, the metal becomes brittle. It then exhibits three directions of low resistance (lines of fracture), which are parallel to the faces of the cubes, and therefore at right angles to each other. If the final product be sheet iron, this, on sustaining a blow, will easily break along two mutually perpendicular directions. The lines of fracture do not follow the lines of contact of the granules, but pass through the granules and follow the cleavage surfaces of the crystals, which, being all in the same direction, offer no opposition to the further extension of the fracture.

If, on the other hand, the individual crystals of the adjacent granules are of different orientation, then the metal, though coarsely crystalline, does not become brittle, and it may therefore happen that a coarse-grained piece of iron will be less brittle than one of finer grain, though under uniform conditions as regards the orientation of the crystals the latter would be the tougher material.

It is particularly worthy of note that, in the above-mentioned case of brittleness of mild steel, the fracture invariably ensues at an angle of 45 degrees to the direction of rolling, and the microscope shows that the orientation of the crystals

in metal that has become brittle through heating to redness is the same. Stead says: "Such material can be bent through an angle of 180 degrees and hammered together, provided the line of flexion be parallel or perpendicular to the direction of rolling, but will break with ease when the bending is made at an angle of 45 degrees to the direction of rolling" (*i.e.* along the lines of fracture).

He also says: "This leads to the conclusion that, just as light produces a latent invisible picture on the photographic plate, so also the act of rolling steel sets up a latent disposition to crystallise in definite directions, which tendency is developed by heating to redness." (This probably has some connection with the breaking-strain theory of Retjö.)

Stead distinguishes between "intracrystalline" brittleness (between the cubical crystals, or along the surfaces of cleavage) and "intragranular" fracture between the crystalline granules. They might also be termed "cleavage fracture" and "granular fracture."

Intragranular fracture follows no definite lines of direction, and is found in a typical form in cast iron. According to Stead, it is the result of a hard membrane or extraneous masses enveloping the granules; or of imperfect cohesion between the granules, the causes of which have not been clearly ascertained.

Although thousands of samples have been examined, no single instance is known of intracrystalline fracture in sheet iron that has not been heated to redness after rolling. The coarse-grained structure appearing after prolonged heating to dull redness is invariably destroyed by heating to 900° C.; the metal then becomes exceedingly tough.

According to Stead, the columnar structure of ferrite, constituted by columnar forms of iron directed from the surface of a bar towards the interior, can probably only occur in the case of steel in which the carbon present at the surface

has been removed by oxidising agents at a temperature lower that 850° C., and under no other circumstances.

On being heated to 900° C., followed by rapid cooling, this form is converted into the normal equiaxial modification, and no method of re-transforming it into the columnar form by heat has yet been discovered.

According to Behrens, the hardness of ferrite lies between 3·5 and 3·7 of Moh's scale.

Mention should also be made of the circumstance that Saniter, in etching nearly carbon-free iron at red heat (by immersion in fused calcium chloride), obtained indications that, at high temperatures, no right angles exist in the crystals of iron, and that therefore, under these circumstances, ferrite does not crystallise in cubes. This would argue the occurrence of dimorphism in iron, and consequently the presence of allotropic modifications of the metal.

(*e*) *Cementite* (according to Howe) is the hardest constituent of carbon steel (H = 6). H. Behrens gives the hardness as between 5 and 7, which Osmond explains by the assumption that the lower degree of hardness is produced by a finer state of division of the carbide, whereas the figures in excess of 6 refer to chromiferous cementite (chrome steel), and therefore to a substance of entirely different composition. The fluctuations in the hardness of cementite may also be ascribed to differences in composition (polymerisation), which subject will be thoroughly discussed in the next section. By reason of this great hardness, cementite can be rendered visible by simple relief polishing with emery paper, in which case it constitutes the portions in relief. Of course it is essential to this end that the cementite should not be so finely distributed throughout the softer matrix as to be beyond the power of definition of the microscope, since in such event chemical methods alone will be capable of revealing its presence.

Cementite is especially well developed in cement steel, from which it takes its name. In this material it forms both isolated groups of large, straight, juxtaposed lamellæ, and similar groups united into a polygonal network. Though at one time both Dr. Sorby and Osmond doubted the identicity of the cementites in different kinds of steel, they are now, in consequence of the analytical results of Ledebur, and microscopical investigations (chiefly by Osmond), all considered as one substance. To be sure, Arnold and Read differentiated two carbides in solution residues (by Weyl's method), the one white and lustrous, the other grey and dull; nevertheless both have the same composition, and the difference is due merely to the lustrous scales being compact, whilst the dull ones are occasionally less densely packed, and wrinkled.

So far as investigations have been carried—even by Osmond—no coloration has been produced by etch-polishing cementite with gypsum and liquorice extract.

Even etching with iodine, eight times repeated, produces no coloration, the cementite remaining silver white under vertical illumination. The same also applies to the effect of 20 per cent. nitric acid allowed to act for at least forty minutes, and of 2 per cent. acid for a more lengthy period.

The researches of H. Behrens and A. R. van Linge on cement steel[1] may also be given in full, since they not only afford information on the composition of cementite, but also represent a typical example of the manner in which such researches should be conducted. These workers, in polishing cement steel, noticed crooked figures of a harder substance, which proved capable of better development by the aid of coloration and etching. "Since it was readily feasible to continue the etching to a depth of 0·3 mm., attempts were made to isolate this hard substance. In a preliminary experiment with fuming hydrochloric acid, a yield of 2 per cent.

[1] Fresenius, *Zeits. f. analyt. Chemie*, vol. xxxiii. p. 513.

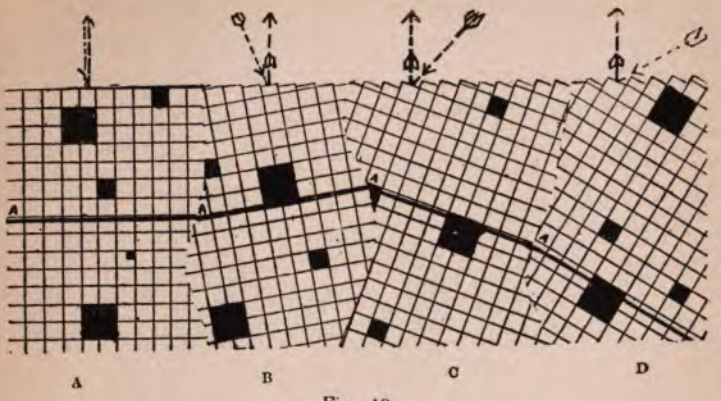
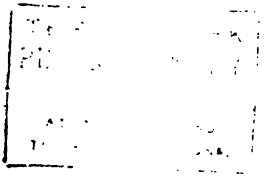


Fig. 49.

Fig. 50.
Crystallised iron carbide.
Magn. 150 linear.

Fig 51.
Martensite and Cementite,
wrought steel
(1,24% C.)
hardened at white heat.
Smooth polished
(Magn. 20 lin.)

Specially printed for Scott, Greenwood & Co.



the crude steel) was obtained; but sulphuric acid, diluted
a fourfold volume of water, proved a more suitable re-
nt, the yield being raised to 3·5 per cent., and later, after
necessary precautions had been ascertained, increased to
per cent. During the first two hours a faint odour of
rocarbons could be detected; later, when the detachment
metallic particles commenced, the liberated gas exhibited
ecidedly disagreeable smell; and finally the odour of
ic became so strong as to forcibly recall phosphuretted
rogen, although the steel had been prepared of best
edish iron and wood charcoal.[1] The detached particles of
al, which contained a slight admixture of carbon, were
arated from time to time by agitation with water and
anting. The fragments of iron were eliminated by warm-
along with 5 per cent. sulphuric acid, the residual metallic
der being repeatedly shaken up with water after the
lution of hydrogen had ceased, and the turbid liquid
red off, in order to break down the fragments of carbon
carry them away. Repeated boilings with distilled water
re finally necessary to eliminate the last traces of acid and
uble iron compounds, which would have discoloured the
paration in drying. In the first and second dryings a
ong smell of garlic was again noticeable; and the dried
idue appeared as a coarse pale-grey powder with high
tallic lustre, recalling pulverised spiegeleisen. It was
racted by a steel magnet almost as readily as coarse filings
bar iron. The degree of hardness was found to be a little
her than that of apatite, though less than that of window
ss; it may be set down as between 5·2 and 5·3. At the
ne time, the substance was so brittle that it could easily
ground to a fine powder in an agate mortar. Under

[1] The author thought of acetylene, but further researches by Behrens have
wn that this substance does not appear, on which account the latter ascribes
evil odour to the decomposition of a silicide.

the microscope only metallic spangles and filaments were discernible, but no crystalline granules.

"A preliminary qualitative examination gave a high percentage of carbon and a low percentage of phosphorus; sufficient, however, to be readily detectable by means of ammonium molybdate and nitric acid, in the extract from a fusion with sodium carbonate and potassium nitrate. The quantitative examination made by van Linge gave 6·6 per cent. of carbon.[1] If the mean carbon content of crude (knife and spring) steel be taken as 0·74 per cent., there is an accumulation of nine times that quantity in the hard spangles, and, in view of the fact that, under favourable conditions, the yield of hard spangles is about 5 per cent. of the raw material, the carbon content of the intermediate substance is 0·4 per cent. at the most. Even this percentage is shown to be too high by the test for hardness. On examining etched sections in the course of this test, under the microscope, the value H = 5 is found for the crooked twigs and branches, 3·5 to 3·7 for the intermediate substance, that is to say, the same hardness as iron containing 0·1 to 0·2 per cent. of carbon. The deviation is elucidated by the more precise microscopical examination of sections that have been etched to a depth of about 0·1 mm., this procedure revealing the presence of a duller and fainter relief, partially corresponding to the outlines of cubes, between the more decidedly projecting lustrous lines. On carrying the etching further, this fainter portion becomes more vague, and disappears. In this case we have to do with a subordinate accumulation of carbon, in consequence of which the carbon content of the intermediate substance is reduced to one-half, or even less, and we must assume that the treatment with acid first attacks the soft iron, and then, simultaneously with the evolution of the noxious gases, the fine, hard strips and scales.

[1] Therefore exactly corresponding to the formula Fe_3C.

"A point worthy of note is the high carbon content of the sparingly soluble carbide, which is equal to that of the white iron richest in carbon, which latter iron it also resembles in colour and hardness. Whether the whole of the carbon is actually in combination could not be determined, owing to the small quantity of the substance; probably a small portion is present in admixture in the graphitic state, since a little carbon is separated on treating the crude steel with acids. Whether the phosphorus plays any part in the formation of the carbide rich in carbon must also remain undecided, though it may be regarded as certain that an accumulation of phosphorus occurs therein. The phosphorus content of Danemora iron may be put down as 0·02 per cent., and the total amount of hard carbide in crude cement steel as 10 per cent.; if, as seems probable, all the phosphorus passes over into the latter, this would correspond to a phosphorus content of 0·02 per cent. in the carbide."

From these researches it follows that cementite cannot always be regarded as pure iron carbide, but as also liable to contain other compounds (phosphides).

According to the investigations of A. Martens, the cementite in spiegeleisen is in hexagonal crystals. Stead[1] found rhombohedral crystals of iron carbide in a slowly cooled pig iron, poor in manganese (Fig. 48, Plate VI.).

Cementite is magnetic.

(*f*) *Martensite* (Fig. 51, Plate VII., also Figs. 52, 53, and 54, Plate VIII., named by Osmond after A. Martens) is found only in hardened steel. It has long been known, though not its structure. Dr. Sorby, under great reserve, speaks of extremely fine grains. Professor Behrens mentions, in the case of sundry specimens examined by himself, a delicate polygonal network, which, however, is the result of

[1] *Journ. Iron and Steel Inst.*, 1898, vol. i. p. 145; *The Metallographist*, vol. i. p. 336.

superficial decarbonisation. The researches of Martens on more or less annealed steel show the irregular distribution of carbon therein, but not its final structure. Osmond published, in 1891, a photograph of medium hard steel under angular illumination after etching with nitric acid; this exhibited a watered appearance, but was incorrectly explained at the time. Seeing that the grain of fracture is progressively reduced by hardening, until it finally disappears from view in the steels richest in carbon, one would be inclined to assume that hardened steel is amorphous, though actually, as we shall see later, it is decidedly crystalline. Take, for example, steel with 0·45 per cent. of carbon, heat it to 825° C. and harden at 720° C. in a refrigerating mixture at −20° C. Relief grinding shows only an indefinite structure, on account of the fairly regular hardness of the mass; but it is rendered more decided by etch-polishing. We then find slightly depressed groups of needles, or, more correctly, straight fibres arranged parallel, sometimes separated by a granular or vermicular intermediate substance, at others not. Usually three systems of such fibres, parallel to the sides of an equilateral triangle, intersect one another, and, according to Michel Levy, indicate the cubical system of crystallisation. On the other hand, Stead maintains that martensite crystallises in the rhombohedral system.

Martensite revealed by etch-grinding exhibits little or no coloration when treated with liquorice extract, the colour being at most a faint yellow. On the other hand—in conformity with its carbon content—it is stained yellow, brown, or black, even by the first drop of iodine tincture; the fibres always remain clearly visible.

In view of the irregularities produced by staining and etching, one cannot assume martensite to be a primary constituent in the strictest sense.

On the other hand, it retains its form just as well during

the hardening of extra mild steel as in the hardest kinds of steel, with the sole exception that—other things being equal—the needles are the longer and better defined the smaller the proportion of carbon in the metal.

The carbon content of martensite varies between 0·12 and 0·89 per cent., and the coloration assumed on treatment with iodine or nitric acid varies accordingly. In the case of the varieties richest in carbon the coloration is considerable, but never so great as with cementite. Martensite will scratch glass and felspar; it is also magnetic and polar magnetic.

Charpy[1] terms martensite containing a maximum of carbon (0·89 per cent.) "Hardenite," and understands by "Martensite" a form of hardenite diluted with iron.

(*g*) *Austenite* (Fig. 55, Plate VIII.) is the name given by Osmond to a constituent appearing solely in the alloys richest in carbon, and that have been cooled from a very high temperature by immersion in ice water. It contains carbon, probably in solution *per se*.[2] This notwithstanding, it is so soft that it can be scratched by a needle, by apatite, and probably also by fluorspar.

When smooth polished, it has a faint grey appearance, whereas martensite is silver white; in comparison with martensite it is not appreciably deepened by relief polishing. Iodine or nitric acid will impart stains.

As the percentage of carbon increases, so also the proportion of austenite, up to about 1·6 per cent. of carbon, beyond which limit a progressive separation of carbide occurs. Under the most favourable conditions of hardening—which, however, must be determined for each kind of steel—martensite and austenite appear in equal proportion. Austenite is apparently non-magnetic.

[1] *Rev. gén. des Sciences*, 15th January 1897; *The Metallographist*, vol. i. p. 52 *et seq.*

[2] H. von Jüptner, *loc. cit.*

(*h*) *Pearlite* (Figs. 56, 57, Plate VIII.). Sorby first described, under the name "pearly constituent," a binary compound consisting of alternate hard and very soft lamellæ; this was afterwards named "Pearlite" by Howe. Under angular illumination this body exhibits a nacreous iridescence (hence its name), provided the soft and more attackable lamellæ be only ground out to a sufficient depth. After chemical analysis had revealed the presence of cementite (Fe_3C) in all kinds of steel, especially annealed sorts, it was generally concluded that pearlite constitutes a mixture of cementite and ferrite. Is this invariably so? For instance, take a hard steel, containing 1·25 per cent. of carbon, that has been annealed at 750° C., and consists almost entirely of pearlite. This, if ground with colcothar and water on parchment, clearly reveals the alternating lamellæ when illuminated in the usual manner under the microscope. Generally the lamellar structure is readily discernible (as found by Sorby), but is very irregularly developed, and sometimes in such faint relief that the photographic reproduction of the picture, magnified 800 times, is quite devoid of detail. This leads to the assumption that the alternating lamellæ do not always exhibit a difference of hardness corresponding to that of cementite and ferrite. The absolute thickness of the lamellæ may, however, play some part herein, and it may be that the finest of them, having a thickness of only 0·1 μ, cannot offer sufficient resistance to the act of polishing, either because the granules of the colcothar are relatively too coarse, or the lamellæ are too brittle. On prolonging the experiment with etch-grinding, the isolated parts offering a poor resistance to colcothar sustain very little alteration; on the other hand, after a few hundred revolutions, many of them commence to colour, the shade passing from yellow to brown, purple, and blue. At each separate moment the colours of the individual islets are very different; moreover,

on one and the same islet, according to the orientation of the lamellæ, the patina may be coherent and exhibit all varieties of bands, or else interrupted, the unstained lamellæ being depressed or in relief. Similar results are obtained with iodine. Now, under these circumstances, no coloration is furnished by cementite or ferrite, either with iodine or liquorice extract. Consequently we are in presence of a new primary constituent, which has been named "Sorbite" by Osmond, in honour of Dr. Sorby, one of the earliest pioneers of metallography.

The foregoing facts show that the alternating lamellæ of pearlite may consist of cementite and sorbite, sorbite and ferrite, or of two differently coloured varieties of sorbite; or, finally, of cementite and ferrite, with or without an intermediate filling of sorbite. Osmond believes that ferrite and cementite never come into absolute contact, though he is unable to demonstrate this on account of experimental difficulties. Moreover, from what is known of the cementite content of steel, and of the surface it presents in a preparation, it is probable that a portion of the cementite in sorbite is so finely divided that even a magnifying power of 100 is insufficient for its recognition.

Pearlite is found only in annealed steel. In specimens polished in relief, pearlite stands up in comparison with ferrite.

In addition to the scaly pearlite described above, Osmond distinguishes another modification of this constituent, to which he gives the name of granular pearlite. The only difference between them is that the latter has a granular structure, and is consequently destitute of the iridescence exhibited by the lamellar variety; for which reason Oliver Arnold has objected to the application of the name pearlite to the granular modification, and proposes that it should be called sorbite. However, since this latter name is already

appropriated to another substance, and would therefore produce confusion, its adoption cannot be recommended.

Lamellar pearlite appears in particular beauty in steel that has been allowed to cool very gradually from a high temperature without disturbance. Granular pearlite, on the other hand, is found in steel that has been forged down to a comparatively low temperature, or merely re-heated to a lower temperature.

(*i*) *Sorbite* (Osmond) occurs merely as a structural element of pearlite. Its microscopical reactions have already been described; but nothing further is known as to its chemical composition, and, in the absence of a method of separation, this problem is not easy of solution. That it contains carbon is, however, certain from the fact that it is stained by iodine tincture. In view of the circumstance that the whole of the carbon in the steel is not entirely confined to the cementite, it seems probable that the carbon of sorbite is a kind of hardening carbon (see Book III.), which is liberated in the gaseous form by Müller's method, and gives a comparatively slight stain with nitric acid. Furthermore, it appears to represent a kind of intermediate stage between martensite and cementite.

(*k*) *Troostite* (Osmond) occurs most clearly defined in medium hard steel. Take, for example, a metal containing 0·45 per cent. of carbon, heated to 825° C. and hardened at 690° C. When this is ground with colcothar on a parchment backing, it exhibits granules in relief, a number of depressions, and, between the two, intermediate cord-like layers of medium hardness. After etch-grinding, it is found that the hard granules consist of martensite, and the depressed portions of ferrite; whilst the intermediate bands exhibit coloration, though less rapidly than sorbite, and the colours resemble irregular marbling. Their structure is almost entirely amorphous, slightly granulated, and warty.

Fig. 5

Martensit
Cemen

(Forged st
1·24 % C,
and harde
735 °
Etche
Magn. 1

Fig. 55.

Austenite and Martensite.

(Cement steel with 1·50 % C, heated to 1050 ° and hardened in ice water). Etched. Magn. 1000.

Fig. 5

Marten

(Forged ste
0·45 % C, h
825 ° and h
at 720
Etche
Magn. 1

Fig. 56.

Perlite.

(Steel with about 1·00 % C, forged and annealed at 800 °). Polished in relief. Magn. 1000.

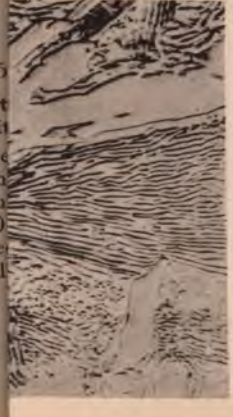


Fig. 5

Martensit
Ferri

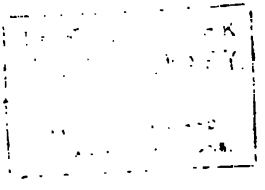
(Forged ste
0·20 % C, h
900 ° and h
at 720
Etche
Magn. 1

Fig. 57.

Perlite and Cementite.

(Cement steel with 1·50 % C). Etched. Magn. 1000.

Specially printed for



A similar effect is produced by iodine tincture.

Osmond named this substance Troostite, after the well-known French scientist Troost.

It is evident that troostite forms an intermediate stage between soft iron and hardened steel. However, like sorbite, it has up to the present only been determined by its microscopical reactions, and its exact chemical composition still remains to be ascertained.

According to the foregoing, the following characteristic properties are available for the recognition of micrographical structural elements.

1. Relief polishing shows up the hardest constituents, especially cementite, in relief.

In order to obtain a clear view of the structure of ferrite, it is often advisable to employ Vienna lime as well as colcothar in relief polishing.

2. Etch-polishing with Vienna lime and liquorice extract, or with ammonium nitrate, produces the following results:—

(*a*) *Unstained.* — Ferrite, cementite, martensite, and austenite.

(*b*) *Stained.*—Martensite, austenite, troostite, and sorbite.

Martensite assumes merely a yellowish coloration, and is recognised by its crystalline habit. A less experienced observer might confound martensite with pearlite, since both of them are iridescent under angular illumination, and, besides, their structural elements may be of equal size. Differentiation is, however, an easy matter, the needles of martensite being straight and intersecting, whilst the lamellæ of pearlite are crooked and do not intersect. Ferrite and cementite differ greatly in point of hardness, on which account the former appears as depressions, the latter in relief. Troostite stains to a smaller extent, and more slowly than sorbite. The great distinction between them, however, is that the former only

accompanies martensite, whilst the latter is associated with cementite and pearlite.

3. Etching with iodine tincture gives the following results:—

(*a*) *Unstained.*—Ferrite and cementite.

(*b*) *Stained.*—Sorbite, troostite, martensite, and austenite.

Of the structural elements making their appearance when other fundamental substances besides carbon and iron are present, we will now merely refer to high-grade manganese steel and nickel steel. These exhibit neither pearlite nor martensite. Manganese steel chiefly consists of polyhedral granules, intersected by one to two systems of cleavage, which approximate more closely to austenite in behaviour. After prolonged cooling, the granules are enveloped in cementite, but when the cooling proceeds rapidly the cementite has no time to separate out, and is therefore undiscoverable. Nickel steel behaves in a very similar manner. That the assumption of a resemblance between this form and austenite is correct, will be seen later in treating of the behaviour of such steels during cooling, etc.

In special steels certain hard crystalline depositions not infrequently occur, which are now classed as "cementite"; but since their composition is often different from that of ordinary cementites, it will soon be necessary to invest them with another appellation. Particulars regarding these and other depositions in iron alloys will be given in Book III.

CHAPTER IV

RELATION BETWEEN MICROGRAPHICAL COMPOSITION, CARBON-CONTENT, AND THERMAL TREATMENT OF IRON ALLOYS

LEAVING out the non-metallic elements (cavities and slag) appearing in iron alloys, we find that the nature and quantity of the other structural elements differ both according to the composition and thermal treatment of the alloys themselves.

Graphite and free cementite are found only in alloys rich in carbon, free ferrite only in those poor in carbon. Martensite and austenite appear solely in hardened iron, whilst pearlite is found only in iron that has been slowly cooled or annealed.

Pearlite or martensite may occur in association with free ferrite or free cementite, whereas the two latter structural elements never appear together.

All these phenomena speak in favour of the formation of these various forms from liquid or solid solutions, as we shall see more clearly later on. Nevertheless it will already be easily comprehended that, from a concentrated solution of carbon and iron, only the first-named will be separated (as graphite), whilst only iron carbide (as cementite) will separate from a concentrated solution of iron carbide in iron; and that consequently ferrite and cementite cannot be separated simultaneously. According to this view, we must assume martensite to be a solid solution of iron carbide in iron, in support of which we shall have numerous other reasons to

advance later. Pearlite then corresponds to the eutectic mixture of ferrite and cementite, and as a matter of fact Ponsot, in 1859, showed with eutectic mixtures of coloured salts and ice that these mixtures consist of alternate crystals of ice and salt, the latter either in the anhydrous or hydrated condition.

In many instances the microscopical investigation of the manner in which the deposition of the structural elements in question has been effected, affords additional information. Special interest attaches in this connection to the researches of H. Behrens on the microscopical structure of metals and alloys, for which reason we will consider the same more closely.

In the case of grey iron the combined carbon is distributed unequally; this is indicated by the irregular coloration produced by pickling, the unequal attack in etching, and the irregular hardness after heating to redness and quenching. Fine-grained varieties of grey iron, when annealed up to reddish brown, exhibit rectangular crystalliths composed of violet-tinged spheroids and a yellow or orange-coloured network. The darker annealing colour belongs to the more easily and readily annealed iron, rich in carbon; and since this fuses at a lower temperature than iron poor in carbon, the spheroids cannot very well be globuliths, nor the lines of the network mother liquor, although both give rise to this impression in the microscopical picture. Etching with weak nitric acid or chromic acid imparts a dark colour to the spheroids, and considerably corrodes the network. The most instructive pictures are afforded by etching with hydrochloric acid. Acid of sp. gr. 1·2 may be allowed to act for three minutes, but stronger acid, which gives clearer pictures, must be swilled off after thirty seconds, the etching being repeated if necessary. The portions rich in carbon remain white and lustrous in the acid, whereas iron poor in carbon is grey and

dull. It thus becomes evident that in most specimens of coarse-grained grey iron, and in many samples of fine-grained iron, the portions poor in carbon are associated with the occurrence of graphite scales, whereas other specimens show in addition a decidedly crystalline structure, or incipient traces thereof, in the parts where the graphite scales are less plentiful. Since the carbon-content of grey iron (0·5 to 1·5 per cent.) differs little from that of steel, a capacity for hardening and a certain workability would be expected; and experiments directed to that end have shown that both properties appertain to all kinds of grey iron, though not to the same extent. Coarse-grained grey iron (Lowmoor iron) seems, by rapid testing after quenching, to be just as soft as before; but if a quenched sample be crushed to coarse powder it will be found to contain hard granules that are absent in the powder from unquenched specimens. The forging capacity is very low.

Medium and fine-grained grey iron can be more uniformly hardened and more easily forged, without attaining the flexibility and elasticity of forged cement steel, which it often exceeds in hardness.

Sections of graphite scales are usually accompanied, on one or both sides, by a washed-out edging, which, on being tested by oxidation or etching, proves to consist of iron poor in carbon. This is a phenomenon corresponding to the light aureoles surrounding microliths and crystalliths in many blast-furnace slags and vitreous rocks. It might be assumed that spontaneous deposition has occurred in both cases, and that the clouding crystalline particles in the immediate vicinity of larger crystals are absorbed and attracted by the latter. Against this hypothesis comes the circumstance that, in addition to a majority of dull glasses with clear aureoles, there is also known an important minority of clear glasses, coloured by iron, exhibiting colourless aureoles.

It is more probable that, as Behrens believes, the presence of these halos can be explained by the behaviour of supersaturated solutions towards crystals of the salt that is dissolved in excess. Even this, however, does not seem to be quite accurate, since the introduction of crystal nuclei into supersaturated solutions merely effects the crystallisation of the excess of the salt, and nothing further.

White iron, rich in carbon, can be converted into grey iron by fusion at a high temperature. Slow cooling plays a part in this process; nevertheless, the deposition of graphite seems to be brought about by the absorption of silicon. The microscope affords little clue to this operation.

The microchemical examination of the above-mentioned aureoles teaches that they contain silica; whether in larger proportion than the intervening portions richer in carbon is unknown, though this is probably the case, since, according to Wedding,[1] the particles of iron, not infrequently embedded in the graphite scales, often contain more silicon than the main body. It may be considered as certain that the deposition continues to occur until the grey iron is fully solidified, since otherwise the formation of the aureoles poor in carbon would be impossible. Moreover, this also follows from their fairly regular distribution through the mass of the grey iron, whereas, if deposition had ceased at an earlier period, the graphite would necessarily, by reason of its lower specific gravity, accumulate at the surface of the metal.

We shall learn more about this process later on.

The occurrence of graphitic particles of iron in groups in mottled pig iron, moreover, indicates that a separation of the iron into two different parts may occur before the deposition of graphite has concluded.

Again, not merely the chemical composition, but also the thermal treatment of the iron alloys, has an important influ-

[1] *Handbuch der Eisenhüttenkunde*, 2nd edition, vol. i. p. 29.

ence on the nature of the structural elements appearing therein.

Thus the deposition is complete at 1130° C. If a pig iron be suddenly cooled down from a higher temperature to below this point, the deposition of graphite will be suddenly interrupted, and the iron will therefore contain less graphite than if it had been cooled slowly. If the iron had contained so little graphite that deposition would not occur above 1130° C., then the suddenly cooled metal would not contain any graphite, and would become white, whereas if cooled slowly it would have been grey or mottled.

The processes in solid metals are very similar, except that in these the conversion temperatures of the different structural elements mostly differ according to the composition. This applies to the conversion of austenite into martensite, the deposition of cementite or ferrite from martensite, and finally the conversion of martensite into pearlite.

If the metal be slowly cooled or warmed to above these conversion temperatures, the conversion will occur, whereas this will not be the case if the cooling be effected suddenly (by quenching) to below the conversion temperature.

This behaviour forms the basis of the two phenomena known respectively as the hardening and annealing (softening) of steel, and which will be fully discussed later on.

Mention has already been made, in Chap. II. Book I., of critical points, temperatures, and temperature zones; and in Chap. VII. it was stated that such critical points occur not only in liquid solutions, but also in solid solutions. It was also shown that solution curves are obtained by connecting analogous critical points.

Fig. 58 represents these curves in accordance with the latest determinations made by Roberts-Austen[1] for iron-

[1] *Fifth Report to the Alloys Research Committee of the Inst. of Mech. Eng.*, 1899.

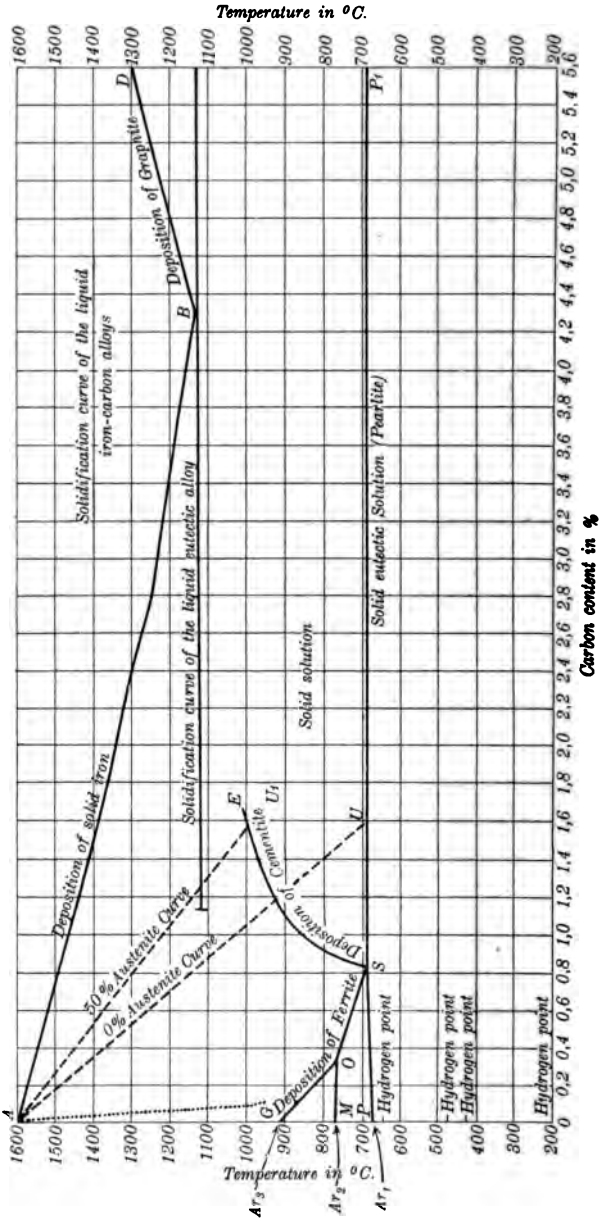

Temperature in °C.
Solidification curve of the liquid iron-carbon alloys
Deposition of Graphite
Deposition of solid iron
Solidification curve of the liquid eutectic alloy
50 % Austenite Curve
0 % Austenite Curve
Deposition of Cementite
Solid solution
Solid eutectic Solution (Pearlite)
Deposition of Ferrite
Hydrogen point
Hydrogen point
Hydrogen point
Temperature in °C.
Carbon content in %

FIG. 58.

carbon alloys. A B represents the solidification of iron, it being left undecided whether the deposition is one of pure iron or of a solid solution of carbon in iron. B D corresponds to the deposition of graphite, and a B c to the solidification of a eutectic alloy of 4·3 per cent. of carbon and 95·7 per cent. of iron.

The critical points occurring in solid iron-carbon alloys correspond to the following curves:—

G O represents the critical points marked A_3, at which ferrite is deposited from martensite during cooling.

M O represents the critical points marked A_2, at which also ferrite is deposited from martensite. The horizontal course of this line causes it to appear a eutectic one, but we shall afterwards find another explanation therefor.

O S corresponds to the critical points marked $A_{2,3}$; here also a deposition of ferrite occurs.

S E, corresponding to a number of critical points, which have not received any special designation, is caused by the deposition of cementite from martensite. Osmond first proved this curve, not by critical temperature determinations, but by microscopical investigation. If, for example, a steel with 1·5 per cent. of carbon be hardened as much as possible, say by immersion in ice water, the resulting microscopical picture differs considerably in accordance with the hardening temperature. When the hardening temperature is 1100° C. or higher, only traces of cementite are found; if 800° C., then cementite is present in abundance; consequently the deposition of the iron carbide must commence at a temperature residing between these limits. On heating a rod of the same steel to 1100° C. at one end, whilst the other end remains below dull red heat, and then hardening in ice water and examining a longitudinal section under the microscope, the cementite is found to be lacking at the end exposed to the greatest heat. It commences to appear at a

certain point corresponding to a definite quenching temperature, the proportion increasing with the falling hardening temperature to a certain value depending on the composition of the steel; and, finally, martensite is replaced by pearlite. Now, so far as the occurrence of a critical point in the deposition of cementite and martensite is concerned, it must not be forgotten that this deposition goes on between wide limits of temperature, and that the resulting evolution of heat is only slightly appreciable, and therefore easily overlooked. Nevertheless, it was observed on several occasions and with different kinds of steel, both by Osmond and Roberts-Austen. That it is not always found is due to the fact that we have here frequently to do with supersaturated solutions, in which the presence or absence of depositions depends on the presence or absence of crystal nuclei.

P S P^1 corresponds to the conversion of martensite into pearlite, P S representing the critical point A_3, whilst S P_1 represents the critical points $A_{1, 2, 3}$.

Finally, the line A U—drawn by the author on the basis of two reports by Osmond—is the 0 per cent. austenite curve, *i.e.* embraces temperatures at which the conversion of austenite into martensite is just complete. A similar hypothetical line, A U_1—the 50 per cent. austenite curve (which, however, is based on only a single report by Osmond)—would represent the appearance of equal proportions of austenite and martensite.

According to the foregoing, austenite and martensite—which therefore, in our view, are solid solutions of iron carbide, or of elemental carbon in iron—occur in association. We have already seen that in the case of mottled iron a separation of the mass into two differently composed parts is probable, even whilst solidification is in progress; since otherwise the frequent accumulation of alternate white and grey portions in such iron would be inexplicable. In this

case we have apparently to do with the simultaneous appearance of several, only partly miscible liquids, in the same manner as actually occurs in certain aqueous solutions. Thus, according to G. S. Newth,[1] when a strong aqueous solution of ammonia (sp. gr. 0·880) is shaken up with a saturated solution of potassium carbonate, two separate layers are formed, just as in the case of oil and water. At the ordinary temperature the potassium carbonate dissolves about 37 per cent. (vol.) of the ammonia solution, whilst the latter takes up about 6 per cent. of the potassium carbonate solution. The solubility of each solution in the other increases as the temperature rises; and the curves of solubility intersect at 43° C., above which temperature the liquids are miscible in all proportions. The mutual solubility is also increased by the addition of a little water. An addition of 12·9 per cent. of water causes a cessation of the special phases above 10° C., whilst with an addition of 18·1 per cent. of water the liquids are rendered miscible in all proportions at all temperatures above zero C. When cooled below this critical temperature, however, the clear solution immediately becomes turbid, and separates into two liquids.

Naturally, the same alterations are produced by warming as by cooling, but in the opposite direction; nevertheless, the critical points appearing in this case (calescence points) do not exactly coincide with these occurring during the cooling process (recalescence points), the former being always a little the higher of the two. The calescence points are indicated by Ac (Ac_1, Ac_2, Ac_3, $Ac_{1,2}$, $Ac_{1,2,3}$), the others by Ar (Ar_1, Ar_2, Ar_3, $Ar_{1,2}$, and $Ar_{1,2,3}$).

Pure iron exhibits only the points A_1 and A_2; alloys with 0–0·25 per cent. carbon show the points A_1, A_2, and A_3; between 0·25 and 0·82 per cent. carbon there occur only two critical points ($A_{1,2}$ and A_3); and steel with more than 0·82

[1] *Pro. Chem. Soc.*, 5th April 1900.

per cent. carbon has only one definite critical point ($A_{1,\ 2,\ 3}$), which, however, always appears.

The designations $A_{1,\ 2}$ and $A_{1,\ 2,\ 3}$ imply respectively double and triple points, in which the points A_1 and A_2 or A_1, A_2, and A_3 coincide. The reasons favouring this assumption will be evident later on.

It must also be mentioned that the conversions in question are not effected at exactly a given temperature, but within certain temperature limits, and that the critical points represent the maxima of evolution (or absorption) of heat within the said limits of temperature.

Reference should also be made to another remarkable behaviour of iron alloys very poor in carbon, which may best be studied in an example observed by Howe and Sauveur, namely, a steel with 0·09 per cent. of carbon—

MICROGRAPHICAL COMPOSITION OF STEEL WITH 0·9 PER CENT. OF CARBON.

Hardening Temperature.	Martensite, per cent.	Ferrite, per cent.	Cementite, per cent.	Pearlite, per cent.
Above Ar_3	77	23	0	0
Between Ar_3 and Ar_2 . . .	27	73	0	0
Between Ar_2 and Ar_1 . . .	11	89	0	0
Below Ar_1, or when cooled slowly	0	90	0	0

Above Ar_3 the steel consists of 77 per cent. of martensite and 23 per cent. of ferrite; the martensite, however, containing only a very small proportion of carbon (or iron carbide). When etched with iodine or nitric acid it assumes a pale yellow coloration, and is not very hard, since it is readily scratched by a needle. Between Ar_3 and Ar_2 the steel consists of 27 per cent. of martensite, distributed in irregular granules throughout the matrix of free ferrite. The martensite of this specimen is much harder than that of the previous one, and assumes quite a dark colour when

etched. It is very hard, forms a decided relief when polished on a soft underlay, and cannot be scratched by a needle. Between Ar_2 and Ar_1 the proportion of martensite undergoes still further diminution, since it forms only 11 per cent. (vol.) of the entire mass. During the retardation Ar_2 about 15 per cent. of the ferrite present in the martensite at higher temperatures separates out, thus increasing the amount of free ferrite to 89 per cent. After quenching below Ar_1, the structure is found to consist of 10 per cent. of pearlite and 90 per cent. of free ferrite. During the critical point Ar_1 the 11 per cent. of martensite present above that temperature disappears, 10 per cent. of pearlite and 1 per cent. of ferrite being formed; and the microstructure of the same steel, after slow cooling, is similarly constituted. Consequently quenching below the critical zone neither alters the temperature nor the relative proportions of the constituents; and this applies to every kind of steel.

According to Sauveur, above Ar_3, 0·12 part of carbon can unite with 99·88 parts of iron (it being assumed, for the sake of simplicity, that the steel consists exclusively of iron and carbon), or, in round figures, 1 part of carbon to 800 parts of iron, to form martensite. The martensite can no longer absorb ferrite; and if the steel contain less than 0·12 per cent. of carbon, the unabsorbed excess is present as free ferrite. Between Ar_3 and Ar_2 we find 0·25 part of carbon to 99·75 of iron, or 1 part to 400. In this temperature zone martensite can no longer absorb ferrite, and any excess present remains free. Between Ar_2 and Ar_1 the amount of ferrite capable of uniting with carbon to form martensite is still smaller, namely, 0·5 per cent. carbon to 99·5 per cent. iron, or 1 part to about 200. Any further quantity present is unabsorbed. Here we have a point which might be termed the *saturation point of carbon for iron.*

From this, however, follows the notable fact that iron

alloys very low in carbon may still contain free ferrite even above Ar_3; and this is confirmed by the following observations of Osmond in the case of steel with 0·14 per cent. carbon, 0·045 per cent. silicon, 0·018 per cent. sulphur, 0·01 per cent. phosphorus, and 0·19 per cent. manganese.

Heating and Hardening Temperature, Degrees C.	Martensite, per cent.	Ferrite, per cent.	Approximate C-content of the Martensite, per cent.	Parts Fe per 1 part C.
Heated to 960 C., quenched at 670 C. (between Ar_1 and Ar_2)	14	86	1·0	99·00
Heated to 960 C., quenched at 770 C. (between Ar_2 and Ar_3)	24	76	0·58	171·41
Heated to 960 C., quenched at 820 C. (mean of Ar_3)	46	54	0·30	332·33
Heated and quenched at 1000 C.	61	39	0·23	433·78
Heated and quenched at 1340 C.	90	10	0·16	624·00

This compels the assumption that in the case of very soft steel there must exist above Ar_3 a critical point (Ar_4), which, however, is apparently difficult to observe on account of the inconsiderable evolution of heat. The curve corresponding to this series of points is shown in its presumptive course by the dotted lines in Fig. 58; it connects the curve G O with the fusing point A of pure iron.[1] Anyway, there is also a probability that the small quantities of ferrite remaining when iron poor in carbon is heated above Ar_3 would disappear were the substance heated long enough to Ar_3, since these reactions proceed very slowly in solid solutions. Further investigation is therefore necessary before any final conclusion can be formed.

The manner in which the microstructure of steel containing large percentages of carbon changes with the hardening temperature, can be gathered from the following data collected by Sauveur (and partly by Howe):—

[1] The author has already referred to this in his paper, "The Solution Theory of Iron and Steel" (*Journ. Iron and Steel Inst.*, vol. i.).

STEEL WITH 0·21 PER CENT. CARBON.

Hardening Temperature, Deg. C.	Position of Hardening Temperature with regard to Critical Point.	Microstructure. Martensite, per cent.	Ferrite, per cent.	Pearlite, per cent.
880	Above Ar_2	100·0	0	0
836		100·0	0	0
797		100·0	0	0
761		100·0	0	0
733		100·0	0	0
714	Commencement of Ar_2	97·20	2·80	0
713		86·00	14·00	0
698	Middle of Ar_2	70·20	29·80	0
652	Between Ar_2 and Ar_1	35·20	64·80	0
650		30·80	69·20	0
633		32·00	68·00	0
626		31·50	68·50	0
620	Commencement of Ar_1	30·00	68·40	1·60
600	End of Ar_1	4·00	78·50	17·50
595		2·00	75·80	22·20
575	Below Ar_1	0	78·90	21·10
532		0	76·80	23·20
512		0	77·00	23·00
340		0	77·40	22·60
263		0	75·20	24·80
200		0	76·40	23·60

STEEL WITH 0·35 PER CENT. CARBON.

Hardening Temperature.	Martensite, per cent.	Ferrite, per cent.	Cementite, per cent.	Pearlite, per cent.
Above Ar_2	100·0	0	0	0
Between Ar_2 and Ar_1	56·0	44·0	0	0
Below Ar_1	0·0	50·0	0	50·0

STEEL WITH 0·8 PER CENT. CARBON AND OVER.

·er cent.	Hardening Temperature.	Martensite,[1] per cent.	Ferrite, per cent.	Cementite, per cent.	Pearlite, per cent.
0·80	Above Ar_1	100·0	0	0	0
	Below Ar_1	0·0	0	0	0
1·20	Above Ar_1	94·0	0	6·0	0
	Below Ar_1	0·0	0	8·0	92·0
2·50	Above Ar_1	80·0	0	20·0	0
	Below Ar_1	0·0	0	23·0	77·0

[1] And also partly of austenite, which was still unknown at the time these experiments ere made.

As can be seen, the alterations in the microstructure generally coincide exactly with the critical points. The only exceptions are the deposition of ferrite in iron very low in carbon, and the conversion of austenite into martensite, or deposition of free cementite from the latter, as already mentioned.

CHAPTER V

THE MICROSTRUCTURE OF SLAGS

For the sake of completeness we will now proceed to the consideration—even if only in a cursory fashion—of the microstructure of slags. The most complete investigations on this point are those of J. H. L. Vogt of Christiania,[1] which well deserve to be thoroughly studied by all who are interested in this subject.

As in the case of rocks, the microscopical examination of slags is conducted with thin sections of the material.

The minerals discovered in slags by Vogt (a few of which do not seem to be present in natural rocks) are almost exclusively developed as skeleton crystals, mainly on account of the rapid cooling inevitable in practical smelting. If, however, as the result of a combination of special circumstances, the stage of cooling be protracted over a number of hours, or even extended to days, perfect crystals are formed, as the labours of other mineral synthesists have shown.

The following minerals were detected in slag, by Vogt :—

A. Pyroxene Group ($\mathring{R}O \cdot SiO_2$).

Augite, chiefly in Swedish blast furnace slags, which not infrequently contain free, fully-developed crystals of the

[1] *Verhandlungen der k. schwed. Akad. d. Wissenschaften*, 1884, vol. ix. No. 1 ; *Jernkontorets Annaler*, 1885, "Beiträge zur Kenntnis der Gesetze der Mineralbildung in Schmelzmassen," Christiania, 1892.

mineral. It often appears in the typical forms shown in Figs. 59, 60, 61, and 62, Plate IX. The crystals are monoclinic, and the composition is as follows:—

$$m((Mg,Fe)O,CaO,2SiO_2) + n[(Mg,Fe)O,(Al,Fe)_2O_3,SiO_2].$$

Sections through the crystals frequently reveal the forms shown in Figs. 63, 64, and 65, Plate IX.

A distinction exists between non-aluminous and aluminous augite. The former varies in composition between—

$$3CaSiO_3 + MgSiO_3 = CaMgSi_2O_6 + Ca_2Si_2O_6$$

(corresponding to a maximum content of lime) and—

$$CaSiO_3 + 3Mg(Fe)SiO_3 = CaMg(Fe)Si_2O_6 + Mg_2(Fe_2)Si_2O_6$$

(with a maximum of MgO and FeO).

The other has the formula—

$$RSiO_3 + n\,Al_2(Fe_2)Si_3O_9.$$

Augite is deposited when the composition of the fused mass approximates to the formula $RSiO_3 + n\,Al_2Si_3O_9$; whereas, when the composition is $RSiO_3 + n\,Al_2O_3$, other minerals (olivine, melilite, and gehlenite, magnesian mica, plagioclase, etc.) make their appearance.

Alumina and ferric oxide seem to play very subordinate parts in the pyroxenes.

Enstatite (MgO-pyroxene) may occur in bisilicate slags rich in MgO; it is one of the rarest of slag constituents, crystallises in the rhombic system, and may be expressed by the formula $MgOSiO_2$. No freely developed crystals have yet been found. Fig. 66, Plate IX. shows two sections, parallel and perpendicular to the axis.

In addition, there is a dimorphous, mono- or asymmetrical $MgSiO_3$ variety.

$MgSiO_3$, like calcium silicate ($CaSiO_3$), is polymorphous, and appears—

1. Alone or with $FeSiO_3$, in the rhombic form, as enstatite.
2. Monosymmetrically or asymmetrically, as magnesia pyroxene.

Wollastonite (CaO-pyroxene) was not detected in free crystals. It crystallises on the monoclinic system, and has the formula CaO,SiO_2. Fig. 67, Plate IX. shows its appearance in sections.

Rhodonite (MnO-pyroxene), in contrast to the two foregoing bodies, easily forms large and well-defined crystals. In accordance with its composition, this mineral (MnO,SiO_2) chiefly occurs in bisilicate slags rich in manganese (mainly in acid Bessemer slag from pig iron rich in manganese). Such crystals are shown in Figs. 68 and 69, Plate IX., the appearance of the sections in Fig. 70, Plate IX.

B. Olivine Group ($(\ddot{R}O)_2 . SiO_2$).

To this group belong—

Forsterite	$(MgO)_2 . SiO_2$.
True olivine	$(MgO,FeO)_2SiO_2$.
Fayalite (iron-olivine) . . .	$(FeO)_2SiO_2$.
Tephroite (manganese-olivine) .	$(MnO,FeO)_2SiO_2$.
Monticellite (calcareous olivine) .	$(CaO,MgO)SiO_2$.

All these minerals crystallise according to the rhombic system, have about the same axial ratio, and are very closely allied both in crystallographical and chemical respects. Pure lime-olivine is not yet known, either native or as an artificial product.

Olivine minerals readily crystallise from melts that are rich in MgO, FeO, or MnO, and have about the composition of singulosilicates. They form often finely developed crystals of the shape illustrated in Fig. 71, Plate IX. In sections they have the appearance shown in Figs. 72 and 73, Plate IX. (fayalite and magnetite), and Fig. 74, Plate IX. (magnesia-olivine).

C. Melilite-Scapolite Group.

The minerals comprised in this group are—

Melilite . . . . $(RO)_{12}(Al_2O_3)_2(SiO_2)_9$;
Gehlenite . . . . $(RO)_3(Al_2O_3)(SiO_2)_2$; and
Akermanite $(RO)_4(SiO_2)_3$, a new mineral comparatively rich in lime and silica; they all crystallise in the tetragonal system.

In the above formulæ, RO chiefly represents CaO w Na_2O and K_2O, in addition to small quantities of Mg FeO, and MnO. The composition of the new tetrago mineral, which is crystallographically and optically all to melilite and gehlenite, corresponds to $(RO)_4(SiO_2)_3$. this case RO is chiefly CaO, with a little MgO, MnO, a FeO.

All these minerals have about the same axial ratio, a crystallise, like the olivines, in one and the same type. Th occur in singulosilicate slags, and are fairly often fou developed as free crystals. Their appearance in sections shown in Figs. 75 and 76, Plate IX.

The most important and characteristic base of the melil series is CaO, though a portion is represented by MgO, Mn FeO, or Na_2O, which latter also facilitate crystallisati During solidification the bulk of the lime passes into t melilite minerals, the main of the magnesia into the matr on which account olivine is frequently deposited sub quently.

When, however, the proportion of MgO is high a the CaO low, olivine is the first mineral to separate o The line of demarcation between the deposition olivine and melilite, with regard to the ratio CaO (M Mg, Fe)O, is independent of the stage of silication of t magma.

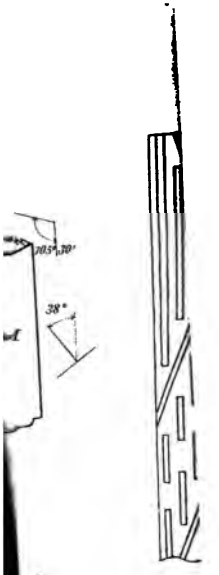


Fig. 6

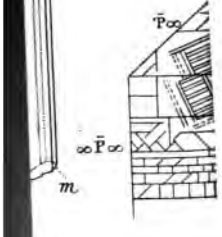
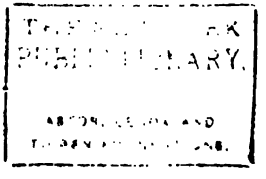


Fig. 75.


PUBLIC LIBRARY.

The melilite minerals must be regarded as mixtures of—

Gehlenite silicate . . . . . $R_3(Al_2)Si_2O_{10}$;
Akermanite silicate . . . . . $R_4Si_3O_{10}$;

and we thus arrive at the following series:—

1. Gehlenite (the most basic member of the group).
2. Intermediate member between gehlenite and the optically negative melilite.
3. Optically negative melilite.
4. Optically isotropic melilite.
5. Intermediate member between optically isotropic and positive melilite.
6. Optically positive melilite.
7. Intermediate member between optically positive melilite and akermanite.
8. Akermanite.

A new hexagonal calcium silicate, forming a group by itself, is found in calcareous slags between 1·45 and 2·5 silicate; microscopical views of sections are shown in Figs. 77 and 78, Plate IX. The composition of this slag constituent is CaO,SiO_2. This silicate, like $MgOSiO_2$, is therefore dimorphous (wollastonite and hexagonal calcium silicate).

Mica is rarely found in slag; and the same applies to willemite $(ZnO)_2SiO_2$.

Spinel (pleonast) of the composition $RO \cdot Al_2O_3$ crystallises in the tesseral system, and occurs in highly basic aluminous blast-furnace slags. It is mostly in the form of octahedra, and is unattacked by hydrochloric acid, sulphuric acid, nitric acid, or hydrofluoric acid. In blast-furnace slag it chiefly occurs as MgO,Al_2O_3.

In the same series are—

Zinc spinel, in which MgO is partly or entirely replaced by ZnO (mostly together with a little FeO).
Hercynite, $FeO \cdot Al_2O_3$, hitherto rarely found in slag.
Magnetite, FeO,Fe_2O_3.

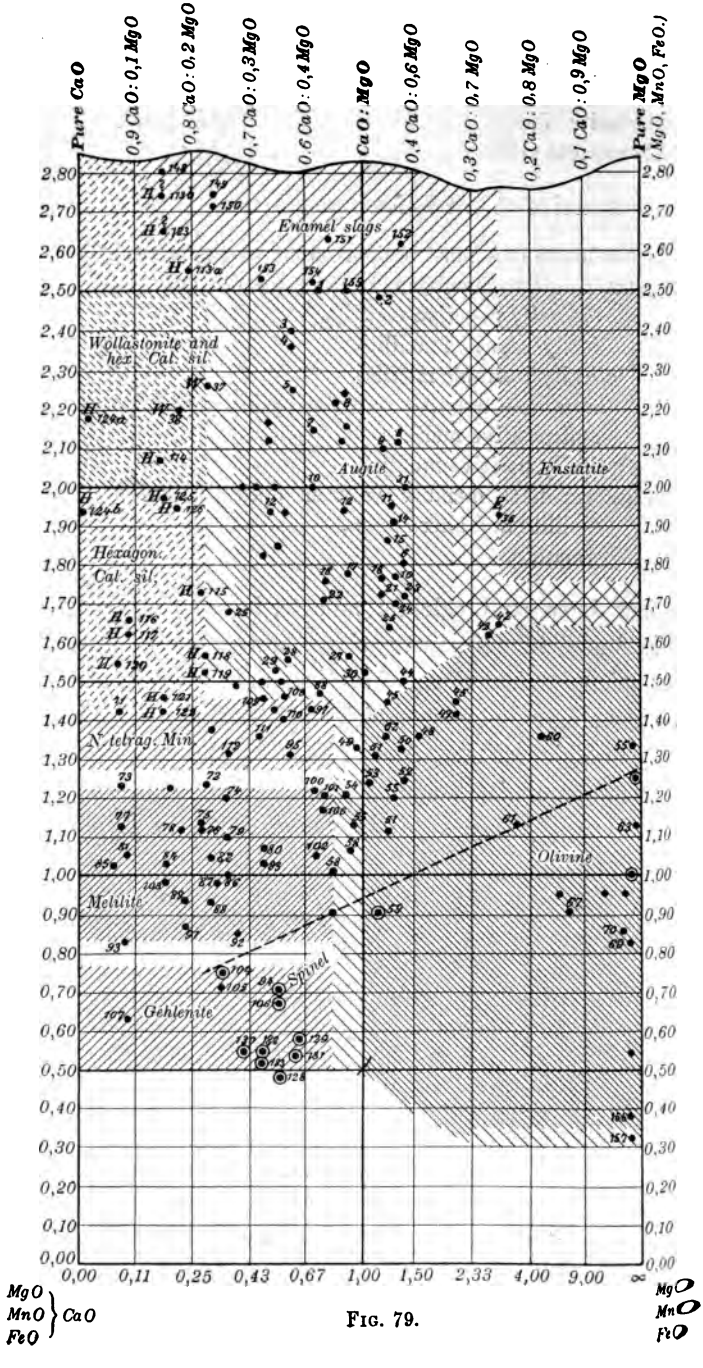

Pure CaO
0,9 CaO: 0,1 MgO
0,8 CaO: 0,2 MgO
0,7 CaO: 0,3 MgO
0,6 CaO: 0,4 MgO
CaO: MgO
0,4 CaO: 0,6 MgO
0,3 CaO: 0,7 MgO
0,2 CaO: 0,8 MgO
0,1 CaO: 0,9 MgO
Pure MgO (MgO, MnO, FeO)
Enamel slags
Wollastonite and hex. Cal. sil.
Augite
Enstatite
Hexagon. Cal. sil.
N. tetrag. Min.
Olivine
Melilite
Spinel
Gehlenite
2,80
2,70
2,60
2,50
2,40
2,30
2,20
2,10
2,00
1,90
1,80
1,70
1,60
1,50
1,40
1,30
1,20
1,10
1,00
0,90
0,80
0,70
0,60
0,50
0,40
0,30
0,20
0,10
0,00
0,00 0,11 0,25 0,43 0,67 1,00 1,50 2,33 4,00 9,00 ∞
MgO
MnO
FeO
CaO
MgO
MnO
FeO

FIG. 79.

Hausmannite, MnO,Mn_2O_3.
Mangano-ferrite, $(Fe,Mn)_3O_4$.
A mineral, CaO,Fe_2O_3 (according to J. Percy and H. Tholander).
Specular iron ore, etc.

In vitreous enamel slags of a degree of silication exceeding 2·5, as well as in very basic enamel slags, numerous globulites occur. The composition of the globulites from the former is assumed by Vogt as $(RO)_2(SiO_2)_3$, whilst that of these in the basic enamel slags is probably (Ca,Mg,Mn)S.

Vogt has arranged the numerous slags investigated by him in a graphical table (Fig. 79), in which the ordinate axis represents the stage of silication, whilst the axis of the abscisses represents the relation between the lime on the one hand, and the magnesia, ferrous oxide, and manganous oxide on the other. He also succeeded in detecting the extent of the limits within which the formation of the several minerals occurs, and in particular their position.

The appearance of phosphates will be dealt with in the Fourth Book.

BOOK III

CHEMICAL COMPOSITION OF THE ALLOYS OF IRON

CHAPTER I

INTRODUCTION

As is well known, the technical varieties of iron are in no wise pure metal, but contain a number of other elements, chief among them being—

A. Principal constituents: Iron, carbon, silicon, sulphur, phosphorus, and manganese.

B. Supplementary associate substances: Oxygen, hydrogen, nitrogen, arsenic, antimony, bismuth, copper, nickel, cobalt, chromium, tungsten, titanium, vanadium, molybdenum, tin, and zinc.

Some of these elements are unavoidable, and then either essential for the purpose in view (*e.g.* carbon), or at anyrate useful (such as silicon and manganese in many cases), or injurious (such as sulphur, and generally phosphorus). Others, again, are designedly introduced for the attainment of definite objects (*e.g.* silicon in grey pig iron, phosphorus in Thomas pig iron, manganese in spiegeleisen, ferromanganese in manganese steel; or like nickel, chromium, tungsten, etc., in special steels).

The most important associate of iron, and the one influencing the manner of its technical utilisation, is carbon.

An attempt has been made to classify the technical varieties of iron according to the proportion of this and other important elements, as well as in accordance with the method of production.

A. Pig Iron. — Cannot be forged, brittle, fuses suddenly when heated. Contains at least 2·3 per cent. of carbon (silicon, phosphorus, etc.).

1. Grey pig iron (a portion of the carbon is deposited as graphite on cooling; the fracture is grey in colour). When the percentage of silicon is large the iron is termed ferrosilicon; used for casting, it is called cast iron.
2. White pig iron (the carbon remains in combination; fracture white). This is harder and more brittle than grey pig iron.
3. Ferromanganese; carboniferous alloys of manganese and iron with high percentage of manganese; the carbon remains in combination on cooling; the fracture is white or yellowish.

B. Forge Iron.—(Capable of being worked, and less brittle than pig iron at the ordinary temperature. Softens when heated gradually to fusing point); percentage of carbon, etc., less than 2 per cent.

1. Bar iron (produced in a pasty condition, contains slag).
   - (*a*) Puddled steel,[1] richer in carbon (about 0·5 per cent. and over), solid, capable of being hardened.
   - (*b*) Bar iron (welding wrought iron), poorer in carbon (less than 0·5 per cent.), less solid, but tougher and more ductile than bar steel; cannot be appreciably hardened.
2. Ingot iron (obtained in a fluid state, free from slag).
   - (*a*) Ingot steel,[1] richer in carbon (0·5 per cent. and over), solid, capable of being hardened.
   - (*b*) Ingot iron, poorer in carbon (less than 0·5 per cent.), less solid, but tougher and more ductile than the corresponding steel; cannot be appreciably hardened.

This proposed classification, which, however, has failed to secure general adoption, was drawn up at the time of the Universal Exhibition in Philadelphia, 1876, by a committee composed of the following members:—

Germany, H. Wedding; England, J. Lowthian Bell; France, L. Gruner; Austria, P. Tunner; Sweden, Richard Akerman; United States, A. L. Holley and Thomas Egleston.

[1] In the Prussian State Railways the term steel is confined to such kinds of iron as exhibit a tensile strength of at least 50 kilogs. per sq. mm. (71,114 lbs. per sq. inch).

Greater favour has been accorded to the following classification:—

I. Non-Forgeable Iron (pig iron). — Readily fusible, melting suddenly when heated. Carbon content, 2·3 to 5 per cent. (up to over 7 per cent. in the case of ferromanganese).

- *A.* Grey pig iron. With graphite.
  Carbon content, 3·5 to 4 per cent. (of which 0·3 to 0·5 per cent. combined). Fusing point, 1100° to 1300° C. (according to Pouillet, 1100° to 1200°; Gruner, 1180°; Ledebur, 1275° C.).
  Specific gravity—
  Dark grey . . 6·635 to 7·275.
  Light grey . . 6·915 to 7·572.
  Termed cast iron when employed for casting.
- *B.* White pig iron. Without any large proportion of graphite.
  Carbon content, 2·3 to 5 per cent. Fusing point, 1050° to 1200° C. (according to Pouillet, 1050° to 1100°; Ledebur, 1075°; Gruner: spiegeleisen, 1055°; white pig iron, 1122° C.).
  Sp. gr. 7·056 to 7·889.
  Harder and more brittle than grey pig iron.
  1. Spiegeleisen. Carbon content, 4 to 5 per cent.; manganese content, 4 to 20 per cent. and over.
  2. White steel and ordinary white iron. Carbon content, 2·3 to 4 per cent.; manganese content, 1 to 5 per cent.
- *C.* Ferromanganese. Without any important proportion of graphite.
  Carboniferous alloys of iron and manganese, with 30 to over 80 per cent. of manganese, and up to over 7 per cent. of carbon.

II. — Forgeable Iron (wrought iron and steel). — Difficult to fuse; gradually softens when heated. Carbon content, 0·04 to 2·3 per cent.

- *A.* Wrought iron. Cannot be appreciably hardened. Carbon content, 0·04 to 0·6 per cent. Fusing point, 1800° to 2250° C.[1] (according to Dainelle, 1587°; Pouillet, 1500° to 1600°; Carnellay, 1804°; Pictet, 1600°).
  Sp. gr.: rods, 7·352 to 7·912; wire, 7·794 to 8·100.
  1. Bar iron. Prepared from the pasty condition, containing slag (blooming furnace, finery, puddled, and truss iron).
  2. Ingot iron. Obtained from the liquid condition, free from slag (Bessemer, Thomas, reverberatory furnace, or Siemens-Martin Pernot iron, etc.).
- *B.* Steel. Capable of being hardened. Carbon content, 0·6 to 2·3 per cent. Fusing point, 1300° to 1800° C.[1] (according to Pouillet, 1300° to 1400°; Gruner, 1350° to 1400°; Ledebur, 1375° C.).
  Sp. gr.: puddled steel in rods, 7·826 to 8·082; ingot steel, 7·400 to 7·825.
  1. Puddled steel. Obtained from the viscid condition, containing slag (finery, cement, and blistered steel).
  2. Ingot steel. Obtained from the fluid state, free from slag (Bessemer, reverberatory furnace, or Siemens-Martin carbon steel. Cast steel, *i.e.* re-melted crucible cement steel, etc.).

[1] According to more recent observations, these figures are decidedly too high.

With the ingot iron and ingot steel series must also be associated the so-called special steels, which, in addition to carbon, contain other elements (manganese, chromium, nickel, tungsten, etc.) added by design.

The aforesaid associated substances present in iron are only in part in the elemental condition, partly in chemical combination therein; and even those present in the former state in technical varieties of iron frequently assume different forms. In fact, the investigations performed within recent years have demonstrated that all the constituents of iron alloys appear in at least two different forms therein.

It would, naturally, be a matter of particular interest to be able to ascertain exactly the intimate composition of the iron alloys, since this is the chief factor influencing their mechanical and physical properties. Unfortunately, however, progress in this direction has not advanced beyond the initial stages, as we shall see in the following pages.

CHAPTER II

CONSTITUENTS OF IRON ALLOYS

Carbon

According to the experience gained up to the present, iron that contains nothing but carbon exhibits the following characteristic chemical components:—

A. Pure carbon, separating out as such, in the form of—

(*a*) Graphite, crystallising in the well-known hexagonal scales, and separating out before, during, and immediately after solidification;

(*b*) Tempering carbon (also known as graphitic tempering carbon), *i.e.* amorphous carbon, which is deposited within the already solidified metal when the same is subjected to prolonged heating at high temperatures; and

(*c*) (According to Rossel and Frank) possibly the diamond, which, however, (according to Werth and Moissan) cannot be deposited at any other time than during the brief interval when the metal is in course of solidifying, this being the sole period when the essential conditions prevail.

B. Carbon in the form of chemical compounds or in solution—

(*a*) Carbide carbon, chemically combined with iron to form iron carbide, Fe_3C;

(*b*) Hardening carbon, as to the chemical nature of which divergent views still exist.

The chemical character of the various forms of carbon is

revealed by their behaviour towards acids and other reagents, as the following table will show :—

1. Graphite crystallises on the hexagonal system, and is unattacked even by boiling strong acids (not too concentrated nitric acid).

2. Graphitic tempering carbon behaves like graphite in presence of acids; is black, lustreless, and quite amorphous; burns more readily than graphite.

3. Diamond crystallises regularly and behaves like graphite towards acids. Its preparation in a pure state is a highly complex process (see Frank, *Stahl und Eisen*, vol. xvii. p. 670).

4. Carbide carbon. When heated with strong acids this modification of carbon is disengaged in the form of hydrocarbon. If the specimen of metal be dissolved in very dilute hydrochloric or sulphuric acid at the ordinary temperature, with exclusion of air, the "carbide" is left behind as a grey or brown mass, which, according to Müller,[1] consists of granules with a silvery lustre, and igniting spontaneously at a relatively low temperature on drying. On dissolving the sample of iron in cold dilute nitric acid of sp. gr. 1·2, there forms a flocculent brown residue, which gradually dissolves on heating, without any evolution of gas, and furnishes a brown solution that suffers but little alteration on prolonged boiling (Osmond and Werth).[2]

5. Hardening carbon occurs, in traces at least, in all kinds of iron.[3] On dissolving the iron in dilute hydrochloric or sulphuric acid, this carbon is given off as strong smelling hydrocarbon gas; when cold nitric acid of sp. gr. 1·2 is employed, there forms at first a black deep residue, which, when shaken up briskly and left for a few minutes, dissolves

[1] *Stahl und Eisen*, 1888, p. 292.

[2] *Ann. d. Mines*, 8, vol. viii. pp. 5–84.

[3] Probably an illusion, iron carbide itself being slightly decomposed by very dilute acetic acid.

without any visible evolution of gas, but, if the solution be gradually heated to 100° C., is slowly liberated in the gaseous state, the dark coloured solution becoming progressively lighter (Osmond and Werth).[1]

To facilitate detailed description of the different forms of carbon occurring in iron, they may be conveniently divided into two groups:—

A. CARBON IN THE ELEMENTARY FORM

(a) *Graphite*

As already mentioned in Book II., graphite separates out in the form of thin plates—often several millimetres in length and breadth, and sometimes decidedly hexagonal—in solidified iron. According to Behrens, it is also found in the form of powder (probably very minute scales). In microscopical sections it assumes the form of distorted lines, not infrequently intersecting at nuclear points. Behrens reports these as being edged on one or both sides with an attenuated border, which proved to be iron poor in carbon but rich in silicon. Whether this aureole contains a larger proportion of silicon than the intermediate portions richer in carbon could not be ascertained, though probably such is the case, since, according to Wedding,[2] the particles of iron not infrequently embedded in the graphite scales often contain more silicon than the bulk. This phenomenon is apparently connected with the circumstance that the separation of graphite is facilitated by the presence of silicon (and aluminium). The frequently expressed supposition that crystalline silicon is also deposited in addition to graphite, has not yet been confirmed. On the other hand, it would appear that the graphite is always accompanied by small amounts of iron and its

[1] *Loc. cit.* [2] *Handbuch d. Eisenhüttenkunde*, 2nd ed. vol. i. p. 29.

constituents (silicon in particular), as the following analyses show:—

	Scum from a Blast-furnace at Clarence.		Graphite recovered from Drill Turnings, per cent.
	Magnetic portion, per cent.	Non-magnetic portion, per cent.	
Carbon	95.00	54·80	78·32
Iron	1·70	31·20	18·26
Manganese . . .	...	...	1·25
Silicon	...	...	0·75
Phosphorus . . .	...	...	1·42
Sand	3·30	14·00	...
Total . .	100·00	100·00	100·00

That the deposition of graphite from iron rich in carbon is begun whilst the metal is still in a fluid condition, is shown by the appearance of a scum of graphite crystals floating on the surface of the iron: that the same continues to occur after the iron has solidified, is evidenced by the fairly uniform distribution of the crystals throughout the mass of grey pig iron, since otherwise they would rise to the surface and accumulate there.

Manganese and sulphur oppose the formation of graphite: whether—as is alleged by some—a similar influence is exerted by phosphorus, has not yet been definitely proved. The amount of graphite deposited is also influenced by the rate at which iron saturated with carbon is cooled; slow cooling favours, whilst rapid cooling retards, the formation of graphite.

The separation of graphite from solidifying pig iron is accompanied by a not inappreciable disengagement of heat.

The sp. gr. of graphite is 2·17–2·32, its hardness 1·5–1·0. The specific heat increases with the temperature in a very

considerable degree, as is shown by the investigations of F. H. Weber with Ceylon graphite (0·38 per cent. of ash):—

Temperature, ° C.	True specific heat
- 50·3	0·1138
- 10·7	0·1437
10·8	0·1604
61·3	0·1990
138·5	0·2542
201·6	0·2966
249·3	0·3250
641·9	0·4450
822·0	0·4539
977·0	0·4670

Dewar found the mean specific heat of graphite between 19° and 1040° to be 0·310.

Graphite is neither dissolved nor volatilised even by boiling acids, though it is slowly oxidised by boiling nitric acid. Potassium chlorate and nitric acid oxidise it to graphitic acid (Berthelot's graphite oxide), which, when heated, leaves behind a black residue (Berthelot's pyrographite oxide). On heating this oxide with hydriodic acid, hydrographite oxide is formed.

The composition and properties of all these bodies vary according to the nature of the graphite used in their preparation, as is shown in the following table:—

GRAPHITE OXIDE (GRAPHITIC ACID).

Natural Graphite.	Blast-furnace Graphite.	Electrical Graphite (Graphitite).
Scales analogous to mica, pale yellow in colour; converted into a brown mass on cooling; insoluble in all menstrua; composition— $C_{28}H_{10}O_{15}$.	Yellowish green scales that do not cohere on drying; composition— $C_{28}H_8O_{12}$.	Chestnut-brown, not appreciably balling when dried; composition— $C_{28}H_{10}O_{19}$.

PYROGRAPHITE OXIDE.

Natural Graphite.	Blast-furnace Graphite.	Electrical Graphite (Graphitite).
Loose, light, voluminous, moss-like mass, which is formed by heating the foregoing, the reaction being accompanied by a violent, almost explosive, evolution of gas. When treated with an oxidising mixture the bulk dissolves, leaving a small residue of oxide.	Formed when the foregoing is heated, the mass swelling up. When treated with oxidising mixture it dissolves, usually with a slight residue of graphite oxide.	A dense heavy powder produced by heating the foregoing, the mass puffing up. Almost entirely dissolved by oxidising mixture.
HYDROGRAPHITE OXIDE.		
Brown, amorphous; insoluble in all menstrua, does not swell or puff up when heated; re-converted into yellow graphite oxide by the oxidising mixture.	Decomposed by heating, the mass swelling up and liberating iodine vapours; is converted into greenish yellow graphite oxide by the oxidising mixture.	Decomposed without swelling up when heated, and furnished with the oxidising mixture, brown graphite oxide.

According to Hubner and Luzi, mellithic acid $C_6(COOH)_6$ is formed, in addition to graphitic acid, during the oxidation of graphite, the whole of the graphitic acid finally passing over into mellitic acid.

When it is considered that considerable divergences, especially as regards their chemical behaviour, exist between graphite and graphitite, it becomes uncertain whether the graphite appearing in the different kinds of iron is necessarily the same body under all circumstances. In other words, it is quite possible that the constituent we now term graphite in the technical varieties of iron may in the future be subdivided into several different kinds of carbon. For example,

it is possible that constitutional differences of this kind may exist between the graphites separated at different temperatures.

(b) *Graphitic Tempering Carbon*

This constituent of iron alloys is pure amorphous carbon, which behaves like graphite in presence of acids. No chemical separation of graphite from tempering carbon is possible. Its deposition from the metal (really from the hardening carbon) occurs when the latter is maintained for some considerable time at a still indefinite temperature, which is, however, below that at which the deposition of graphite occurs; whether during cooling or re-heating is immaterial. This temperature is higher than that at which the separation of the carbide, to be afterwards described, takes place. Large proportions of manganese hinder the separation of tempering carbon.

In the absence of graphite, somewhat considerable quantities of this second form of carbon can be detected as small black dots, either uniformly distributed or in groups, on the surface of fracture. The sole means by which they can be distinguished from graphite is by their non-crystalline character.

This form of carbon oxidises more readily than graphite: for instance, it is converted into CO by oxygen at red heat, and, according to Forquignon,[1] is volatilised as hydrocarbon when the metal is heated to redness in hydrogen.

Whether tempering carbon is present as pure amorphous carbon in iron, or whether this is first liberated from a compound rich in carbon, by the action of acids, has not been definitely ascertained; but, in the present state of our knowledge, the former hypothesis is the more probable.

When once formed, tempering carbon is unaffected, either by slow or rapid cooling; and it is only by heating the metal

[1] *Ann. de Chim. et de Phys.*, 1886, p. 383.

to very high temperatures that it can be re-converted into hardening carbon.

The tempering carbon of the technical varieties of iron may, according to Weinschenk,[1] be compared with the carbon found in meteorites, and which, on the latter being dissolved by dilute hydrochloric acid, does not volatilise in the form of hydrocarbon, and is only consumed by strong calcination in a platinum crucible. Cohen terms this substance "amorphous carbon."

(c) *Diamond*

According to Rossel and Frank,[2] this form of carbon also occurs in iron. The first-named worker examined special steel by a method devised by Berthelot, dissolving the metal in acid, carefully washing the residue, and oxidising it with nitric acid; then fusing with potassium chlorate after repeated washings, and finally subjecting it to repeated treatment with pure hydrofluoric acid and concentrated sulphuric acid. The resulting powder consisted of microscopically small transparent crystals, characterised by extraordinary hardness. They were able to mark corundum, and burned to carbon dioxide at 1000° C. The steel employed for the rifle barrels of the Swiss infantry regiments, furnished crystals which exhibited a regular octahedral structure under a power of 300 diameters. The same workers afterwards succeeded in demonstrating the presence of black transparent diamonds in iron from a blast-furnace hearth.

H. Moissan, who succeeded in producing artificial diamonds by rapidly cooling molten iron rich in carbon, concludes that graphite and amorphous carbon are formed in iron that is allowed to act on carbon at temperatures between 1100° and

[1] *Ann. d. naturhist. Hofmuseums*, Vienna, 1889, vol. iv. p. 101.

[2] *Schweiz. Bauztg.*, 1896, p. 151; *Stahl und Eisen*, 1896, ii. p. 585; 1897, p. 485.

1200° C., whereas at 3000° C. beautifully crystalline graphite alone is formed. Under certain circumstances (rapid cooling) there may be formed in the latter case a modification, which has the sp. gr. 3·5, will scratch ruby, and behaves just the same as black diamond.

In any case, the formation of diamond can only occur when the separation of the carbon takes place under heavy pressure (Werth).

It may also be remarked, in passing, that diamonds have been found in meteorites.

The hardness of the diamond is 10, and its sp. gr. is between 3·49 and 3·53.

B. COMBINED CARBON

Whereas elementary carbon is either not at all or only slowly attacked by dilute hydrochloric, sulphuric, or nitric acid, even at boiling temperature, combined carbon furnishes more or less volatile decomposition products with the former reagents, either already in the cold or on boiling, whilst dilute nitric acid gives organic compounds containing hydrogen, oxygen, or nitrogen.

According to the views hitherto generally current, this combined carbon may be divided into two classes, which we will now proceed to describe in detail.

(a) *Carbide Carbon*

According to Osmond ("Théorie céllulaire," etc.), this carbide carbon—which Rinman terms "cement carbon," and which is also known as "incandescence carbon," or "chemically combined carbon"—separates out from the metal containing the hardening carbon (to be described later on) at between 660° and 780° C. in the case of iron alloys rich in carbon, and even to some extent at still higher tempera-

tures. On the metal being heated to a temperature rather higher than the deposition temperature of the carbide carbon, the latter is re-converted into hardening carbon.

The combination of this portion of the carbon with the iron, forms crystalline substances of a high degree of hardness (cementite) in the solidified metal. Manganese and tungsten hinder the formation of the carbide; silicon, in large proportions, diminishes the formation by favouring the deposition of graphite. Slow cooling facilitates, whilst rapid cooling (hardening) retards, the deposition of carbide. When hardened steel is heated, the separation of carbide begins already at 100° C. Consequently the ratio between carbide carbon and the total carbon depends both on the composition of the metal and on the conditions of cooling.

When heat is applied in conjunction with strong acids, the carbide carbon is liberated in the form of hydrocarbons. On dissolving the metal in very dilute hydrochloric or sulphuric acid, the above-named carbon is left behind as a grey or brown mass, which, according to Müller,[1] consists of a number of silvery lustrous granules, which, on drying, ignite at a relatively low temperature. When the sample of iron is dissolved in cold dilute nitrite acid (sp. gr. 1·2) the carbide carbon remains as a flocculent brown substance, which, on the application of heat, gradually dissolves without any evolution of gas, and imparts to the solution a brown colour that undergoes very little alteration when boiled (Osmond and Werth).[2]

Many attempts have been made to facilitate the separation of the carbide in various ways, which we will now briefly describe.

J. O. Arnold and A. A. Read[3] dissolved five kinds of

[1] *Stahl und Eisen*, 1888, p. 292.
[2] "Théorie céllulaire."
[3] *Proc. Chem. Soc.*, 3rd May 1894.

steel (with between 0·96 and 0·06 per cent. of carbon) according to a modification of the Weyl and Binks method (dissolving by means of the electric current), and obtained residues containing the following proportions of the total carbon :—

From steel with about	1	per cent. of carbon	.	92 per cent.
„ „	0·5	„ „	.	87 „
„ „	0·25	„ „	.	78 „

The loss they do not place to the account of the hardening carbon, but assume that, independently of the electrolysis, a matrix poor in carbon is dissolved by the hydrochloric acid used. The residue was collected on a flat filter, washed with alcohol and ether, dried *in vacuo*, and analysed. It was found to be iron carbide of the formula Fe_3C. According to these workers, this "normal carbide" occurs in two chemically identical forms. Normal steel furnished a greenish black powder, probably pulverised crystalline carbide, partially decomposed by the solvent. A carbide in an extremely fine state of division was obtained from hardened steel; whilst carefully hardened steel yielded silvery white scales of Sorby's "pearly substance," the composition of which exactly corresponded to the formula Fe_3C.

Abel[1] employed potassium bichromate and dilute sulphuric acid as the solvent, the addition of chromic acid being intended to hinder the evolution of hydrogen, and therefore the escape of hydrocarbons. He obtained by this means a black heavy pulverulent residue, which did not ignite on exposure to the air, and which was for the most part decomposed by hot hydrochloric acid, volatile hydrocarbons being formed. Hardened steel gave 4·7 per cent., annealed steel as much as over 90 per cent., of the

[1] *Eng.*, 1885, xxxix. p. 150.

total carbon in the residues, the composition of which was as follows :—

	Iron, per cent.	Carbon, per cent.	Water, per cent.
Cold-rolled cement steel . . .	92·77	6·92	0·93
Softened ,, ...	91·80	7·04	1·32
Annealed ,, ...	89·92	7·23	2·28
Cold-rolled other steel	90·87	7·12	2·09

The ratio iron : carbon approximately corresponds to the formula Fe_3C with 93·33 per cent. Fe and 6·67 per cent. C. Hence Abel deduces the existence of the carbide Fe_3C already surmised by Karsten in cold-rolled or annealed steel.

Müller[1] suffuses the pulverised metal with 10 per cent. sulphuric acid in a glass beaker, and leaves it to stand for a few days under a slow current of illuminating gas. The residue is collected on a tared filter, washed with a large quantity of boiling water, followed by ether and alcohol, dried in a current of illuminating gas at 120° C., and finally left to cool in a similar atmosphere. This preparation is so pyrophoric that it ignites spontaneously when only just warm to the touch. The substance contains chemically combined water, with which it parts at incandescence in illuminating gas, the resulting product being then far more readily soluble in dilute acid. The water content of the carbide ranges from 0·5 to 1 per cent.; the carbon varies between 6·6 and 7·7 per cent., the mean being 7·2 per cent. From his researches Müller deduces the existence of a carbide of the formula Fe_3C.

The carbide is only attackable with extreme difficulty by copper salts; moderately concentrated hydrochloric or sulphuric acid dissolves it, hydrocarbons being liberated, and a slight residue left corresponding nearly to the formula FeC_8.

[1] *Stahl und Eisen*, 1888, p. 291.

Completely hardened steel—as prepared by Müller, by heating small quantities of turnings to incandescence in a platinum crucible, and quenching the whole in cold water—gives no residue when dissolved in cold dilute sulphuric acid; white pig iron, however, under the same conditions, leaves a considerable amount of residue.

On dissolving completely hardened steel in dilute acids, the whole of the carbon volatilises in the form of hydrocarbons. If, on the other hand, solution be effected with exclusion of nascent hydrogen, the carbon is left behind as such.

The investigations of H. Behrens and A. R. van Linge have already been referred to in Book II.

The most exhaustive investigations of all in connection with the carbide in question were those of F. Mylius, F. Foerster, and G. Schoene.[1] They first dissolved softened tool steel (carbon content 1·30 per cent.) by the electrolytic method in a bath of concentrated zinc sulphate with 0·1 per cent. of free acid, a plate of zinc being employed as cathode. With a current of 1 ampere per sq. cm. at the anode, no evolution of hydrogen could be detected. The loose grey corrosion layer appearing on the steel was brushed off under water, washed with water, alcohol, and ether, and dried in an atmosphere of hydrogen. Microscopical examination showed the resulting grey powder to consist of lustrous acicular or laminar crystals. Analysis gave a carbon content of 7 and 9 per cent., and about 90 per cent. of iron. In presence of dilute hydrochloric or sulphuric acid the powder gave no liberation of hydrogen, and therefore contained no free iron.

Now, whereas the steel from which this substance was obtained is completely soluble in hot hydrochloric acid, small quantities of an undissolved carbonaceous substance were invariably left on treating the carbide in the same manner.

[1] *Zeits. f. anorgan. Chemie*, 1896, vol. xiii. p. 38.

Consequently the iron carbide seems to have been decomposed by the electric current.

A preliminary attempt to extract steel of low carbon content with normal sulphuric acid, showed that the evolution of hydrogen ceased entirely after the lapse of a week. There remained behind a dark porous, spongy mass, in which spangles, with a metallic lustre, could be detected under the microscope. The residue, washed with water and dried, contained 3·5 per cent. of carbon. It partly dissolved, with evolution of gas, in boiling hydrochloric acid, leaving a residue of 30 per cent., which, on combustion, gave 7 per cent. of carbon; at the same time, a strong sublimate of arsenious acid was formed. The rest consisted of silica; small quantities of iron, copper, manganese, and phosphorus being also present.

The far purer tool steel already used above was next thoroughly annealed, treated with dilute acids at the ordinary temperature, and left exposed thereto, air being excluded, until the evolution of hydrogen had entirely ceased. The residue, ground in a porcelain mortar, was washed on a tared filter with water, alcohol, and ether—air being, as far as possible, excluded—and dried at 120° C. in a current of hydrogen. The following results were obtained:—

No.	Acid Employed.	Duration of Expt. Days.	Weight of Substance, Grms.	Residue.		Percentage of Carbon in Residue.
				In Grms.	In per cent. of Steel.	
1	400 cc. 2-normal sulphuric acid .	7	10·30	1·619	15·7	7·03
2	200 cc. 2-normal sulphuric acid .	9	10·09	1·694	16·8	6·52
3	500 cc. normal sulphuric acid .	10	10·19	1·645	16·2	6·54
4	500 cc. normal hydrochloric acid	14	10·31	1·494	14·5	7·18

80 to 84 per cent. of the total carbon in the steel

remained in the residues, whilst 16–20 per cent. was converted into volatile carbon compounds. In addition, the residue contained small quantities of hydrogen and oxygen, as well as organic impurities, as is shown by the analysis of residue No. 2—

FIG. 80.

Carbon . . .	6·5 per cent.
Iron	89·6 „
Manganese . .	0·5 „
Silicon . . .	0·3 „
Copper . . .	0·2 „
Hydrogen, oxygen, loss	2·9 „
	100·00

The percentage of carbon in the residues fluctuated about 10 per cent.; moreover, the steel was not sufficiently pure, and, in addition, the residue was rapidly oxidised, under the influence of damp air, during grinding. In washing with acid, the resulting iron oxide is dissolved, and the residue may then appear richer in carbon than it originally was.

It also appears that the carbide deposited when access of air is permitted is only partially soluble in hot hydrochloric acid, —similar to the carbide prepared by electrolytic methods,—whilst a slight carbonaceous residue is left in addition to silica.

To obtain carbide residues that are perfectly soluble in

hot hydrochloric acid, the steel must not only be treated with acid, but the residues must also be washed and dried with exclusion of air, use being made of the apparatus shown in Fig. 80. The vessel A having been charged with the steel and acid, the air is rapidly displaced from the tube B by hydrogen, the tube C being immersed in water. By means of the three taps it is easy to subsequently replace the saturated solution by fresh acid from the dropping funnel. The completion of the reaction is indicated by the cessation of hydrogen bubbles. In the case of steel discs 2–3 mm. thick, and weighing about 10 grms., the extraction will be complete in about a week if the solution be renewed daily, but in special cases the operation may take several months. The washing of the residue with water, alcohol, and ether is effected by the aid of the dropping funnel, in a current of carbon dioxide introduced into the apparatus through the tube attached to D. For this purpose the three-way tap is particularly useful.

When the steel discs are of metal rich in carbon they retain their shape throughout the entire operation. In such event the washing takes several hours, owing to the very slow rate of diffusion of the solutions in the interior of the porous mass; it is also important to boil the washing liquid, in order to expel contained oxygen to the fullest possible extent. At the close of the operation the ether is displaced by carbon dioxide, which is allowed to escape through the lower end of the apparatus.

The glass cylinder surrounding the vessel A is then filled with warm water, and the temperature is raised to boiling by introducing a current of steam. The drying having been completed in this manner, the hot water is emptied and the carbide residue is then cooled in a current of carbon dioxide, after which it can be removed from the apparatus without danger.

The steel used for the foregoing extractions contained—

Carbon	1·30	per cent.
Manganese	0·30	,,
Silicon	0·21	,,
Phosphorus	0·11	,,
Sulphur	0·05	,,
Copper	trace	
Iron (by difference) . .	98·03	,,
	100·00	

When dissolved in hot hydrochloric acid it left behind a few minute dark flakes containing, in addition to silica, 0·004 per cent. (of the weight of the steel) of insoluble carbon (tempering carbon), *i.e.* only a negligible trace. The probable reason of this is that the steel was heated for several hours at dull red heat and then left to cool. The acid used for the extraction was 2-normal hydrochloric acid (containing 7 per cent. of HCl). The resulting carbide was tested for its solubility in hot 15 per cent. hydrochloric acid in the same apparatus; at first solution proceeded very briskly, then more slowly, and finally the evolution of gas became very sluggish. The residual black flakes amounted to barely 0·1 per cent. of the carbide, and consisted for the most part of silica. The carbide dried at 100° C. sustains barely any loss on being heated to redness in nitrogen; and even when rapidly raised to red heat in hydrogen the loss in weight did not exceed 0·4 per cent. Consequently the residue is free from large quantities of water and oxygen. On the other hand, a liberation of empyreumatic vapours was observed, which may be ascribed to small quantities of hydrocarbons, etc., still adherent to the substance.

The analysis of the carbide residues gave the following results:—

	I.	II.	III.
Carbon	6·50 per cent.	6·56 per cent.	6·44 per cent.
Iron	91·96 ,,		
Manganese	1·10 ,,		
Copper	0·23 ,,		
Silicon	0·02 ,,		
Sulphur	trace		
Phosphorus	,,		
Arsenic	,,		
Nickel	,,		
	99·81		

Hence the preparation contained at least 98 per cent. of iron carbide, along with a little manganese carbide and other impurities.

The iron carbide cooled in carbon dioxide or nitrogen is not pyrophorous, at least when the admission of air is effected slowly, whereas if cooled in hydrogen it glows on the admission of air, and is converted into red ferric oxide without undergoing any change of form. The cause of this phenomenon is probably to be found in occluded hydrogen. When heated to redness in this latter gas, the carbide very slowly loses weight (barely 0·5 per cent. in an hour); after this treatment it is usually no longer pyrophorous.

Dry iron carbide is not attacked by air at the ordinary temperature, but at higher temperatures very readily begins to glow. Damp carbide is oxidised to a brown powder on being exposed to the air for a few hours. On dissolving the resulting iron oxide in hydrochloric acid there remains a dark brown residue distinguishable from carbon by its colour and by containing water. This substance also occurs as an intermediate product when iron carbide is decomposed by dilute nitric acid; but is best obtained by employing for the oxidation of the carbide a cold solution of ammonium persulphate in dilute sulphuric acid. Further particulars respecting this substance will be given later on.

The action of water on iron carbide at the ordinary temperature is nil, and only slight at 100° C. One grm. of carbide heated with 5 c.c. of water in a closed vessel for three hours at 145° C. furnished 0·5 c.c. of combustible gas.

On being heated to 400–430° C. for half an hour in a current of steam and nitrogen, the carbide increased in weight 13 per cent.; the product was black, and contained oxides of iron, in addition to free carbon. The evolved combustible gas consisted chiefly of hydrogen.

When heated to redness in a current of steam the carbide increased in weight 29 per cent. in a quarter of an hour, and swelled up into the form of a loose brown powder consisting of ferro-ferric oxide, the carbon being liberated as gaseous products composed of hydrogen, carbon monoxide, and carbon dioxide, but not of hydrocarbons.

Very dilute acids have scarcely any appreciable action on iron carbide at the ordinary temperature; but at 80° C. even decinormal hydrochloric acid produces an abundant liberation of hydrogen. Concentrated hydrochloric acid dissolves the carbide at a fairly rapid rate in the warm, the carbon passing off almost entirely in the form of volatile products; nevertheless, small quantities of non-volatile or sparingly volatile compounds (insoluble in water, soluble in alcohol, and still more readily so in ether) are invariably observed. On the other hand, the aqueous solution always contains carbonaceous substances, as was demonstrated by L. L. de Koninck and E. Donath. The formation of intermediate amorphous products resembling carbon was not observed in any instance.

The examination of the gas liberated on treating the carbide with 2-normal hydrochloric acid at 80–100° C. by Mylius, Foerster, and Schoene, showed that 92·3 per cent. (vol.) is absorbed by palladium. The remaining 7·7 per cent. exhibited an odour resembling petroleum, burned with a bright flame, and contained complex uncondensable hydrocarbons.

Detonation experiments gave the following results referred to 100 vols. of the original gas—

15·34 vols. of carbon (imagined as in the gaseous state).
126·2 ,, hydrogen.
1·4 ,, nitrogen (presumably from the air).

Turning now to the portion of the gas absorbed by palladium, and considering this as free hydrogen, there remains for the hydrogen combined with the carbon 126·2–92·3 = 33·9 per cent. This evidently agrees very closely with the proportion necessary to combine with the 15·34 per cent. of carbon to form saturated hydrocarbons of the $C_nH_{2n}+_2$ series. (It is very much to be regretted that no attempt was made to absorb the unsaturated hydrocarbons of the olefine series by bromine.)

From these data the approximate composition of the liberated gas would be—

Hydrogen	92·3 per cent.
Hydrocarbon	6·3 ,,
Nitrogen	1·4 ,,

The hydrocarbon remainder had in this case approximately the density of pentane, which contains 15 vols. of carbon (vapour) and 32 vols. of hydrogen condensed to 6 vols. (Pentylene would furnish 15 vols. C + 30 vols. H = 6 vols. of the compound.)

Heating to redness produces no change in iron carbide; when raised to white heat in a current of nitrogen it smelts to a regulus, loose carbon being deposited on the surface. The regulus obtained by Mylius, Foerster, and Schoene was very brittle, with a radial fracture recalling that of spiegeleisen, and contained 4·36 per cent. of carbon, but no graphite. On this regulus being heated to redness, carbide was again deposited.

It has already been mentioned that iron carbide is attacked,

even though slowly, by very dilute acids. The following investigations of Mylius, Foerster, and Schoene, wherein one and the same steel was extracted by acids of different strength, afford numerical data on this point:—

Acid.	Percentage yield of Carbide.	Percentage of Carbon in the Carbide.	
		In per cent. of Carbide.	In per cent. of Steel.
4-normal hydrochloric acid . .	5	6·42	0·3210
2-normal ,, ,, . .	8	6·50	0·5200
½-normal ,, ,, . .	15	6·49	0·9735
4-normal sulphuric acid . .	12	6·71	0·8052
½-normal ,, ,, . .	17	6·64	1·1288
Normal acetic acid . . .	19–20	6·30	1·2600

Dilute acetic acid decomposes the carbide least, and furnishes a carbide containing over 90 per cent. of the carbon present in the steel. Well-annealed steel therefore seems to contain the whole of its carbon in the form of carbide.

The properties and composition of the deposited carbide remain unchanged, whatever the acid and strength of same used for the extraction, and irrespective of whether that operation is conducted at the ordinary or higher temperatures (*e.g.* 45° C.), or whether the steel contains little (0·16 per cent.) or much carbon (1·3 per cent.). From this, Mylius, Foerster, and Schoene draw the entirely justifiable conclusion that iron carbide is a true atomic compound, and not one containing variable proportions of its constituents.

Only in a single particular is the compound Fe_3C said to differ from the carbide isolated from steel, namely, that when decomposed by acids it gives off equal volumes of methane and hydrogen, according to the equation—

$$Fe_3C + 6HCl = 3FeCl_2 + CH_4 + H_2.$$

The workers in question believe that the cause of this may possibly be that the molecular formula of the carbide corre-

sponds to a multiple of Fe_3C, and that the carbon itself forms complex atoms in the molecule of the carbide. This view had already been formulated by L. L. de Koninck, Donath, and the present author, and was confirmed by the subsequent researches of E. D. Campbell and the author (these will be dealt with later).

The foregoing investigations have been confirmed and extended by E. H. Saniter (*Journ. Iron and Steel Inst.*, 1897, ii. p. 115).

By a modification of the method of Binks and Weyl, 14 per cent. (instead of the theoretical 14·5 per cent.) of iron carbide was obtained from a pure steel containing 1 per cent. of carbon. On boiling a sample with diluted nitric acid of sp. gr. 1·2, the greater portion (probably corresponding to the free cementite) proved to be more difficult to dissolve than the fine spangles (presumably derived from pearlite).

Examination of the behaviour of iron carbide at high temperatures gave the following results:—

	Normal Fe_3C.		Heated to 1000° C., and quenched in Cold Water. 1	Heated to 800° C. in Nitrogen. 2	Heated to 1000° C. in Nitrogen. 3		Embedded in MgO and fused in Co. 4
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Silica . .	0·09	...	...	...	...	...	...
Phosphorus	0·004	...	...	...	...	...	...
Sulphur .	0·15	...	...	...	...	...	0·05
Manganese .	...	...	...	...	...	...	...
Iron . .	91·10	91·8	92·6	93·4	93·0	92·7	95·40
Total carbon	6·92	6·68	6·13	6·12	6·13	6·20	4·27
Graphite .	0·19	0·22	0·56	0·40	2·50	2·41	3·05

In the case of No. 1 the carbide was enclosed in a copper tube and heated for five minutes. In Nos. 2, 3, and 4 the heating was prolonged for half an hour, and the samples were left to cool slowly.

These researches indicate a dissociation of the iron car-

bide at high temperatures; nevertheless, it is noteworthy that the amount of graphite deposited in the experiments 1 and 2 was very small in comparison with that furnished by experiments 3 and 4.

Heating to 800°, followed by slow cooling, gave . . .	0·40	per cent.	graphite.
„ 1000° C., and quenching in cold water . . .	0·56	„	„
„ „ and slow cooling .	2·45	„	„
Fusing at about 1400° C., and slow cooling	3·05	„	„

These researches show a few divergences in comparison with the results obtained by Mylius, Foerster, and Schoene, the latter having found no alteration in the carbide under the influence of red heat, whereas, according to Saniter, this is not the case. The fused carbide employed in both cases contained about the same percentage of carbon (4·36 and 4·27 per cent.). Whilst the first-named workers obtained a regulus of white iron, with the structure of spiegeleisen, Saniter obtained grey iron with 3·05 per cent. of graphite. The probable cause of the difference is the fact that the former carbide contained 1·1 per cent. of manganese, the latter only 0·15 per cent.[1]

The behaviour of carbide carbon, or iron carbide, in presence of dilute nitric acid, has already been briefly mentioned, and will be dealt with more fully later on.

It may be not uninteresting to mention that carbide carbon is also found in meteoric iron.[2]

In 1889 Weinschenk found in meteoric iron from Magura, crystals of iron carbide corresponding to the formula (Fe, Ni, Co)$_3$C, and which he proposed to name "Cohenite"; similar

[1] It is not beyond the bounds of possibility that the divergent behaviour of the carbides at red heat may be due to the difference in the percentage of manganese.

[2] An interesting comparison between meteoric iron and manufactured iron has been drawn by O. Vogel (*Stahl und Eisen*, 1896, Nos. 12, 13, and 14).

carbides were afterwards found in meteoric iron discovered in other places. A characteristic feature of the two specimens (from Magura and Wichita) that have been more closely examined, is the highly irregular distribution of the cohenite, which appears in large quantity in some parts, whilst in others it is entirely lacking.

According to Cohen, the properties of this carbide are as follows:—The crystals are long, columnar, and attain in Magura iron a length of 8 mm. and a breadth of 3–4 mm. In Wichita iron they are on the average smaller and thinner; and in this case a vertical tabular habit, and peculiar hacked-about appearance—probably the result of imperfect development—are more frequent and sharply defined. The surfaces are highly lustrous. The crystals are tin white, but frequently of a pale bronze to golden yellow. They are strongly magnetic, and in a high degree brittle, so that their recovery in an unbroken condition is a matter entailing great care. Probably they are distorted regular forms, a condition with which the tendency to cleave would harmonise. (The carbide from artificial iron alloys, however, appears not to crystallise with regularity.) The degree of hardness fluctuates between $5\frac{1}{2}$ and 6, and the sp. gr. is 7·227 or 7·244. They are insoluble in very dilute hydrochloric acid (1 in 20), and can therefore be extracted without difficulty; on digestion with concentrated hydrochloric acid they slowly dissolve, a portion of the carbon being left behind; and in copper-ammonium chloride they dissolve readily, leaving the whole of the carbon as a residue. Analysis furnished the following results:—

Cohenite from Bemdego	.	91·06 Fe;	2·20 Ni;	0·00 Co; 6·73 C.
„ „ Magura	.	89·81 Fe;	2·08 Ni;	0·69 Co; 6·42 C.

whereas the formula $[65Fe, 2(Ni, Co)]_3C$ would correspond to 89·84 Fe, 3·58 (Ni, Co), 6·58 C.

Derby[1] examined the cohenite from the iron from Cañon Diablo, and obtained the following results from two analyses:—

Iron	92·88 per cent.	91·67 per cent.
Nickel and Cobalt .	1·33 ,,	2·43 ,,
Phosphorus . . .	0·48 ,,	0·09 ,,
Carbon . . .	5·33 ,,	6·07 ,,
	100·02	100·26

A different behaviour is exhibited by the meteoric iron from Ruff's Mountain, which does not acquire any permanent magnetism and is said to contain a carbide agreeing almost exactly with the formula Fe_4C.

Forchammer isolated from Greenland telluritic iron (from Niakorna) an iron carbide, for which he assumed the formula Fe_2C. For this compound Shepard proposed the name "Chalypite."

Both occurrences require confirmatory examination.

(b) *Hardening Carbon.*

This modification of carbon receives its name from being found more especially in hardened steel; and as it has also been assumed that the same is uniformly distributed throughout the entire mass, *i.e.* dissolved in the iron, it has been termed dissolved carbon. Apart from the carbon present in austenite, this is the only form of that element contained in iron above a certain temperature. It constitutes the material from which, at certain temperatures, carbide carbon is derived, the formation of which can, however, be hindered by causing the metal to traverse these temperatures as rapidly as possible, *i.e.* by rapid cooling. Such metal is said to be "hardened"; and the characteristic properties of hardened steel depend on the presence of hardening carbon.

[1] *Am. Journ. of Science*, xlix. p. 101.

The carbon in martensite belongs to this category; nevertheless, it would seem that this form of carbon also appears in other morphological constituents of iron and steel.

On dissolving the metal in dilute hydrochloric or sulphuric acid, the hardening carbon is driven off in the form of hydrocarbons; but when cold dilute nitric acid is employed the carbon is at first left behind as a deep black residue, which, however, dissolves rapidly on agitation, or in a few minutes if left at rest, and with evolution of gas on being warmed to 100° C. This will be dealt with again later on.

Opinions on the nature of hardening carbon are still conflicting. Some regard it as elementary carbon dissolved in iron; Howe and Sorby assume it to exist in two definite states of combination, namely—

(*a*) In the proportion 99 : 1 (about corresponding to the formula $Fe_{106}C_5$, or $Fe_{21}C$), of great hardness, appearing in hardened steel; and

(*b*) In the proportion 99·46 : 0·54 (closely approximating to the formula $Fe_{79}C_2$, or $Fe_{40}C$), less hard, and found along with iron carbide (Fe_3C) in annealed steel.

Similarly, John Oliver Arnold distinguishes between [1]—

(*a*) Crystals of slightly impure iron, which are coloured a pale brown on etching, as he supposes in consequence of the presence of small amounts of a carbide having the hypothetical composition $Fe_{10}C$; and

(*b*) Sub-carbide, a compound of great hardness, occurring in hardened and tempered steel, and believed to have the composition $Fe_{24}C$. This substance (martensite and hardenite) is decomposed at a temperature of about 700° C. into Fe_3C and pure iron, heat being evolved. One of its most notable

[1] "On the Influence of Carbon on Iron," Steven's *Indicator*, xiii. No. 2, p. 199.

characteristics is a capacity for becoming permanently magnetic.[1]

More recently, however, the opinion is gaining ground that hardening carbon is nothing more than carbon contained in a definite modification of iron carbide of the empirical composition Fe_3C, dissolved in the excess of iron.

[1] Arnold deduces the existence of the compound $Fe_{24}C$ from the fact that iron with 0·98 per cent. of carbon furnished in different observations a series of critical points—

1. Clearly marked saturation point with reference to the microstructure of normal annealed and hardened kinds of steel;
2. A sharply defined maximum in the curve of recalescence;
3. A point in the compression curves of hardened steel, at which molecular flow absolutely ceases; and
4. A maximum in that curve, which is determined by the percentage of carbon, and the permanent magnetism of hardened steel, as co-ordinates.

In addition were also determined—

5. The maximum of tensile strength (and approximately also the capacity for hardening) in steel containing 0·8–0·9 per cent. of carbon;
6. Maximum difference between the magnetic transformation temperature in heating and cooling; and
7. A minimum of contraction of the steel in its molecular conversion within the zone of critical temperature.

CHAPTER III

CONSTITUENTS OF THE IRON ALLOYS: CARBON—OPINIONS AND RESEARCHES ON COMBINED CARBON.

To supplement the particulars given in the preceding chapter with regard to carbide and hardening carbon, it is necessary to refer to a series of researches performed on iron alloys containing both carbide and hardening carbon.

Eggertz,[1] by treating iron with a solution of iodine in iron iodide, obtained a carbonaceous residue of the empirical composition $C_{80}I + 20H_2O$, with 60 per cent. of carbon.

The carbonaceous residue left behind when iron is dissolved in copper-ammonium chloride was examined by Andrew Blair,[2] who found therein—

Carbon	64·30 per cent.
Water	20·28 „
Oxygen (determined direct)	8·86 „
Chlorine	3·76 „
Nitrogen	0·45 „
Ash	2·45 „
	100·10

A second portion of the residue when heated in a current of hydrogen lost 39·25 per cent. in weight, of which, however, only 12·54 per cent. was moisture. No oily or tarry substances were formed. The residue was non-crystalline,

[1] *Berg- und Hüttenm. Ztg.*, 1863, p. 373; 1875, p. 440; 1381, p. 264.
[2] *Amer. Chem. Journ.*

and contained 57·84 per cent. of carbon, and 2·91 per cent. of ash.

The first analysis would correspond very closely to the formula $3(C_{50}H_{21}ClO_{15})NO_2$.[1] Of this there remains, after heating, a residue of $3C_{45}$, whilst the liberated gases must contain, in addition to 19·5 H_2O, also $3C_5O_{47}3H_8,3Cl$ and N.

Schützenberger and Bourgeois,[2] by repeated treatment with solutions of copper chloride and ferric chloride containing hydrochloric acid, obtained from white pig iron a blackish brown residue, which, when washed and dried at 100° C., gave the formula $C_{11}H_6O_3$ after deducting the silica, graphite, and other impurities. This carbohydrate they named graphite hydrate, and the same is closely allied to Brodie's graphitic acid or Berthelot's hydrographite oxide.

The compound in question rapidly gives off water at 250° C. without undergoing distension; it is briskly attacked by ordinary nitric acid in the warm, and is converted—with liberation of red fumes — into an amorphous red-brown substance that is soluble in nitric acid, alcohol, alkalis, ammonia, and pure water, from which, however, it is precipitable by additions of neutral salts. The ammoniacal solution gives, after boiling off the excess of ammonia, light brown compounds with metallic salts. The average composition of the nitro-product is—

Carbon	52·27 per cent.
Hydrogen	3·52 ,,
Oxygen (difference) . . .	41·45 ,,
Nitrogen	2·76 ,,
	100·00

On heating, this is decomposed, a smell of hydrocyanic acid

[1] Possibly the nitrogen is combined with water, and the chlorine may also be a constituent of the ash.

[2] *Compt. Rend.*, lxxx. p. 911; abstracted in *Chem. Centralbl.*, 1885, p. 387.

being given off, and a black residue left, which latter is converted into a brown product by nitric acid.

The above figures lead to the formula $C_{22}H_{17}(NO_2)O_{11}$ for the substance, which has received the name nitrographitoic acid; Schützenberger and Bourgeois regard this as identical with the substance obtained by Eggertz by the action of nitric acid on iron, which product furnishes peculiarly brownish yellow solutions. On evaporating to dryness the nitric solution containing the chemically combined carbon as soluble nitrographitoic acid, and treating it with alcohol, the silica and graphite remain undissolved, whilst the nitrographitoic acid, etc., passes into solution.

These two observers, in fact, have based on this behaviour a method for estimating graphite and combined carbon.

Zabudsky[1] dissolved in sodium-copper chloride a pig iron containing, apart from 4·104 per cent. of combined carbon, neither graphite, sulphur, nor phosphorus, and found that the dark brown residue, which behaved exactly like a carbohydrate, corresponded most nearly to the formula $C_{12}H_6O_3$. The same composition was exhibited by the residue obtained by decomposing the same pig iron by silver chloride, or by electrolysis. This carbohydrate can be easily nitrated, and readily furnished halogen derivatives, *e.g.* the iodine compound $C_{60}H_{29}IO_{15}$.

Special interest attaches to the investigations conducted by E. Donath,[2] which will therefore be quoted verbatim.

"Spiegeleisen in coarse lumps was treated, first with sodium-copper chloride solution at the ordinary temperature until the originally deposited copper had just re-dissolved (a tedious operation with the quantities taken), afterwards in the cold with a solution of ferric chloride slightly acidified

[1] *Prot. d. Journ. d. russ. phys.-chem. Ges.*, 1882, iii.; *Berichte*, xv. p. 946.
[2] *Oesterr. Zeits. f. Berg- u. Hüttenmesen*, 1895, p. 149.

with hydrochloric acid, and finally digested in the warm with very dilute hydrochloric acid, to make sure of the whole of the iron being dissolved. The brownish black residue was then filtered off, washed with hot water acidified with hydrochloric acid, and finally with hot water until the chlorine reaction had entirely disappeared, after which it was dried at 110° C. until constant.

"The ultimate analysis of the residue gave the following values:—

Carbon.	Hydrogen.
58·13 per cent.	2·52 per cent.
58·39 ,,	2·90 ,,
57·86 ,,	2·80 ,,

nevertheless, it was invariably contaminated with chlorine, although the washing had been continued until the complete disappearance of the silver reaction; but combustion with pure lime in a glass tube gave only 0·03 per cent. of chlorine from the resulting silver chloride; it gave a white incineration residue of 1·28 per cent., which, according to the qualitative examination, consisted almost entirely of silica.

"As can be seen, these results differ from those obtained by Schützenberger and Bourgeois to a not unimportant degree, which is not inexplicable, seeing that it could not be proved in either case whether chemical entities or mixtures were in question. It was, however, proved in both that on treating iron (which, like spiegeleisen, contains chemically combined carbon only) with cupric chloride, or cupric salts generally, the carbon of the dissolved iron remains behind, not in the condition of carbon itself, but as a carbon compound of decidedly organic character, and containing hydrogen and oxygen, the formation of which substance cannot well be explained if it be assumed that the carbon is not combined with the iron in atomic proportions. This brownish black

substance was then converted by means of nitric acid in the manner prescribed by the above-named workers, into the compound to which they have given the name 'nitrographitoic acid,' and exhibited the properties indicated by them."

Donath rightly objected to the name nitrographitoic acid, since it has by no means been proved that the body in question is allied in constitution with graphitic acid, or even that it is a nitro-derivative at all. He therefore proposes to confer on it the less definite name of carbazeic acid.

"Attempts to obtain the substance in the form of crystals from alcohol and other solvents, failed. Ultimate analysis gave the following figures:—

Carbon.	Hydrogen.	Nitrogen.
51·62 per cent.	2·9 per cent.	2·52 per cent.
51·80 ,,	2·97 ,,	2·60 ,,
51·89 ,,	2·86 ,,	

"These values agree considerably better with the results obtained for this compound by Schützenberger and Bourgeois.

"Particularly worthy of note is the high staining power of these solutions of nitrographitoic acid, though this is far surpassed by that of their ammonia salts, prepared by neutralising the acid with ammonia, and driving off the excess of the latter by evaporation in a water bath, a deep, black, lustrous, brittle product being thus obtained. It is undoubtedly to this substance that the characteristic coloration of the steel solutions prepared with nitric acid is due in the application of the 'Eggertz test.' When prepared pure, in the manner described, this substance is indubitably the most suitable for the preparation of normal solutions for the Eggertz test, since it enables comparisons to be made with the same substance, and not merely, as is the case with burnt sugar, coffee, etc., with entirely different substances merely

furnishing similarly coloured solutions, or even with the mixed solution of the chlorides of iron, cobalt, and copper, afterwards proposed by Eggertz. The solution of ammonium nitrographitoate furnishes light to dark brown flocculent precipitates with solutions of metallic salts.

"The barium salt obtained in this way, gave, on analysis, the values—

Carbon.	Hydrogen.	
25·30 per cent.	1·25 per cent.	
24·96 ,,	1·30 ,,	and Ba 41·70 per cent.

The lead salt contained 60·78 per cent. of lead oxide."

On comparing the researches of Schützenberger and Donath, it will be seen that Schützenberger and Bourgeois set up the formula $C_{11}H_6O_3$ for their "graphite hydrate," whereas, according to Donath's report (assuming that only oxygen is present in addition to the carbon and hydrogen ascertained by the ultimate analysis), the formula works out to $C_{58}H_{33}O_{29}$, or perhaps $C_{60}H_{34}O_{30}$. This gives the atomic ratio, carbon : hydrogen = 1·833, or 1·757 and 1·764, and therefore a somewhat defective concordance, which seems to indicate that we have to do with a mixture of several substances, and not with a uniform body.

A comparison of the analyses of the nitro-products gives—

	Schützenberger and Bourgeois.	Donath.
Carbon . . .	52·27 per cent.	51·77 per cent.
Hydrogen . . .	3·52 ,,	2·91 ,,
Nitrogen . . .	2·76 ,,	2·56 ,,
Oxygen (by difference)	41·25 ,,	42·76 ,,

which furnishes, by calculation, the formulæ $C_{22}H_{17}(NO_2)O_{11}$ and $C_{47}H_{32}(NO_2)_2O_{25}$. By doubling the first of these we have $C_{44}H_{34}(NO_2)_2O_{22}$, *i.e.* 3CO less, but H_2 more, than the formula deduced from Donath's analysis, thus supporting our previous hypothesis.

According to Schützenberger and Bourgeois, the formulæ

For nitrographitoic acid . .	$C_{22}H_{17}(NO_2)O_{11}$
and (doubled) graphite hydrate .	$C_{22}H_{12}\quad O_6$
show a difference of . . .	$H_5\,(NO_2)O_5$

whereas, according to Donath, the difference between

Carbazeic acid	$C_{47}H_{32}(NO_2)_2O_{25}$
and "graphite hydrate" . .	$C_{58}H_{33}\quad O_{39}$
is	$-C_{11}H_1\quad O_{14}$
	$+\quad {}_2(NO_2)$

a result equally speaking in favour of a mixture.

Finally, if we compare the analyses of carbazeic acid and its barium salt (according to Donath)—

	Carbazeic Acid.	Barium Salt.
Carbon . .	51·77 per cent.	24·96 per cent.
Hydrogen . .	2·91 „	1·30 „
Nitrogen . .	2·56 „	...
Barium . .	...	41·70 „

and divide the separate values by the corresponding atomic weights, we have—

	Carbazeic Acid.	Barium Salt.
Carbon . .	4·31 atoms	2·08 atoms
Hydrogen . .	2·91 „	1·30 „
Nitrogen . .	0·18 „	...
Barium . .	...	0·27 „

which, when referred to a parity of carbon atoms, gives—

	Carbazeic Acid.	Barium Salt.	Difference.
Carbon . .	4·31 atoms	4·31 atoms	...
Hydrogen . .	2·91 „	2·69 „	− 0·22 atom
Nitrogen . .	0·18 „	...	− 0·18 „
Barium . .	...	0·56 „	+ 0·56 „

an impossible result.

If, however, we remember that, in comparison with the barium salt, the acid must contain twice as many hydrogen atoms as the former has barium atoms, and hence calculate the composition of the acid on the basis of $2{\cdot}69 + 2 \times 0{\cdot}56 = 3{\cdot}81$ atoms of hydrogen, we obtain—

	Carbazeic Acid.	Barium Salt.	Difference.
Carbon . .	5·64 atoms	4·31 atoms	− 1·33 atoms
Hydrogen . .	3·81 „	2·69 „	− 1·12 „
Nitrogen . .	0·23 „	...	− 0·23 „
Barium . .	...	0·56 „	+ 0·56 „

Consequently the acid must contain considerably more carbon than the barium salt, which is equally impossible; it therefore follows that the so-called carbazeic acid is a mixture of compounds, only a portion of which can be precipitated by barium salts.

The analysis of the barium compound gives by calculation the empirical formula $C_{21}H_3(NO_2)O_{17}Ba_3$, which is so complex as to lead to the belief that this compound also is a mixture of different salts.

Osmond and Werth[1] selected a steel of the following composition for solution by the Weyl method:—

Carbon	0·49 per cent.
Silicon	0·075 „
Sulphur	0·024 „
Phosphorus	0·041 „
Manganese	0·37 „

The resulting residue was washed with water, alcohol, and ether, dried *in vacuo*, and weighed on a tared filter. The resulting data, as well as the method of treating the steel, are given in the subjoined table:—

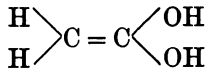
[1] *Mémorial de l'Artillerie de la Marine*, 1887, p. 240.

Condition of the Steel.	Forged and Cooled without Special Precautions. per cent.	Forged and Heated to Redness. per cent.	Hardened in Cold Water. per cent.	Hardened and Annealed. per cent.
Composition of the dry residue—				
Iron	78·40	82·38	52·50	83·22
Carbon	12·00	11·27	18·90	9·92
Water	8·40	6·40	26·07	5·48
Total . . .	98·80	100·05	97·47	98·62
Weight of dry residue in percentage of the weight of the steel	3·31	4·11	1·61	4·14
Percentage of C in the steel—				
Cal. from above figures .	0·397	0·463	0·306	0·41
Estimated direct . .	0·476	0·497	undetermin'd	0·497
Loss of carbon .	0·079	0·034	abt. 0·19	0·087
Absolute weight of dissolved iron, grms.	11·280	9·806	11·520	10·304
Time occupied in dissolving, hours	6	5	5	5

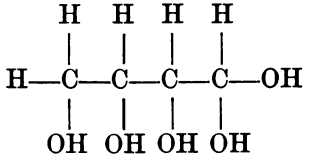
These analyses, as well as the appearance of the samples, show the residue to consist of a mixture of grey magnetic spangles of metallic appearance (apparently undecomposed iron carbide) with a blackish amorphous, gelatinous substance, the latter preponderating in hardened steel, but receding in importance in annealed steel. On calculating the iron content as carbide, and referring the results to equal quantities of carbon, we obtain—

Condition of Steel.	Forged and Cooled without Special Precautions.	Forged and Heated to Redness.	Hardened in Cold Water.	Hardened and Annealed.
Iron carbide . .	$44Fe_3C$	$32Fe_3C$	$30Fe_3C$	$58Fe_3C$
Carbohydrate (?) .	$C_{70}(H_2O)_{44} = 2C_{25}(H_2O)_{22}$	$C_{72}(H_2O)_{56} = 8C_9(H_2O)_7$	$C_{40}(H_2O)_{50} = 10C_4(H_2O)_5$	$C_{35}(H_2O)_{35} = 35C(H_2O)$
Loss of carbon .	C_{18}	C_8	C_{42}	C_{19}

Even though the carbohydrates in the two last columns could be approximately expressed by the formulæ—



and



or in a similar manner, it is still impossible to regard the first two as mixtures of the foregoing, and it is therefore evident that a thorough investigation is still necessary for the elucidation of the matter.

It is, however, interesting to draw into comparison the results obtained by Sir Frederick Abel in his experiments referred to in the preceding chapter. On calculating to atomicities the figures there given, we obtain the following:—

Condition of the Steel.	Cold Rolled.	Heated to Redness.	Annealed.	Cold Rolled other Steel.
	Cement Steel.			
Iron carbide . . .	$32Fe_3C$	$15Fe_3C$	$21Fe_3C$	$28Fe_3C$
Carbohydrate (?) . .	$C(H_2O)_3$	$C(H_2O)$	$C_3(H_2O)_5$	$2C_3(H_2O)_2$

In both series of experiments the composition of the decomposition product of the carbide in annealed steel was the same, namely, $C(H_2O)$, or a multiple thereof.

T. W. Hogg[1] treated one and the same steel (1 per cent. of carbon) in the cast and in the annealed state (in the form of bore turnings) with an excess of dilute nitric acid (sp. gr. 1·2), the vessel employed for the operation being immersed in cold water. In this manner he obtained residues,

[1] *Journ. Iron and Steel Inst.*, 1896, vol. ii. p. 179.

which, after drying over concentrated sulphuric acid, gave the following composition :—

	Annealed.	Cast.
Iron . . .	73·73 per cent.	2·54 per cent.
Carbon . .	8·43 ,,	49·41 ,,
Water . .	7·26 ,,	22·40 ,,
Nitrogen . .	3·20 ,,	8·25 ,,
Oxygen (difference)	7·38 ,,	17·40 ,,
Total .	100·00	100·00

In the above analyses the water obtained on combustion was not calculated to hydrogen; nevertheless, it would appear that a considerable part of the latter is not in combination with oxygen in the substance.

On calculating this analysis in the same manner as before, we obtain—

	Annealed.	Cast.
Iron carbide . . .	$43·9Fe_3C$	$1·5Fe_3C$
Carbon compound .	$3·8C_{14}H_{22}O_{33}N_6$	$0·5C_7H_4O_4N$

These formulæ do not agree at all closely with those obtained previously; only one thing is clear, namely, that the composition of the organic residue from annealed steel is far more complex than it was in the natural condition.

These nitro-products undergo gradual decomposition, even at the ordinary temperature.

Eug. Prost[1] carried out an exhaustive research on the influence of hydrochloric acid on alloys of iron and carbon. He allowed hydrochloric acid, of various strengths, to act on white pig iron of the following composition :—

Iron	85·920 per cent.
Combined carbon . .	2·685 ,,
Graphite	0·465 ,,
Phosphorus	2·700 ,,
Silicon	0·915 ,,

[1] *Rev. Univ.*, September 1890, p. 308; *Berg- u. Hüttenm. Ztg.*, 1891, No. 5, p. 44. According to a private communication, these researches were commenced in the laboratory, and at the instigation of W. Spring of Liége, but completed in the laboratory of L. L. de Koninck.

In all cases he invariably used sufficient acid to dissolve a weight of pure iron equal to that of the pig iron taken, according to the equation—

$$Fe + 2HCl = FeCl_2 + H_2.$$

The concentration of the acid was varied in definite degrees, and each sample was warmed to about 85° C. for six hours on a bath.

A comparison of the residues showed, in the first place, that their appearance varied, and that the total residue (4·19 to 41·33 per cent.) was the greater in proportion as the acid was the more dilute (311·00 to 29·32 grms. HCl per litre). The analysis of the residues further shows that their composition fluctuates; it proves that—

1. The percentage of carbon, hydrogen, and phosphorus increases (C = 2·35 to 12·54 per cent.; H = 0·12 to 2·07 per cent.; P = 0·93 to 11·66 per cent.).

2. The percentage of iron decreases (91·80 to 23·22 per cent.) with the concentration of the acid.

Still more instructive is the calculation of the constituents of the residue to a uniform quantity of pig iron, *e.g.* to 100 parts. This procedure shows that, as the concentration of the acid, and therefore its attacking power, is increased, the residue contains—

Iron	37·947 to 0·972
Carbon	1·047 ,, 0·625
Hydrogen	0·050 ,, 0·087

The results for phosphorus are irregular; the largest proportion of this substance in the residue is furnished by acid of medium concentration.

From these experiments the following conclusions were drawn by L. L. de Koninck:—

"The quantity of acid consumed in the experiment, and the duration of exposure, being known, it is clear that the

pig iron, if it were a perfectly homogeneous mass, would in all cases entirely dissolve, or else leave a residue of constant amount and composition. Since this is not the case, one is compelled to assume that the pig iron contains different compounds, some of which are more readily soluble than the others. This deduction had already been drawn by Halm[1] from the experiments made by him. It is also easy to explain why the residue is greater in the case of weak acid, and why the percentage of (original pig) iron left in the residue diminishes when the concentration of the acid is increased."

This explains also the remaining facts observed, namely—

1. That the amount of carbon in the residue diminishes, whilst the percentage of carbon therein increases, with the concentration of the acid.

2. That the amount of hydrogen in the residue from 100 parts of pig iron, and consequently the percentage of hydrogen therein, increases with the intensity of the action exerted by the acid.

De Koninck assumes that pig iron consists of pure iron, soluble in the most dilute acid, and of three carbides, each of which latter requires the action of a different strength of acid to attack it; further, that — in accordance with facts—the effect of the acid on the various carbides aforesaid is to form different hydrocarbon compounds, some of them gaseous or volatile, others solid at the ordinary temperature. Let P be taken to represent the weight of pig iron employed, a, a′, a″ the weight of carbon in the three carbides, and A, A′, A″ the portion of a, a′, a″ remaining as insoluble organic compounds after the action of the acid on carbide, whilst b, b′, b″ represent the weight of hydrogen fixed by A, A′ A″, and finally c, c′, c″ the weight of iron in the carbide. If the pig iron be treated with so weak an acid

[1] *Ann. de Chem. u. Pharm.*, 129, p. 57.

that the carbide is unattacked, the iron alone will be dissolved, and the residue will contain the three carbides, comprising—

Iron	$= c + c' + c''$
Carbon	$= a + a' + a''$
Hydrogen	$= 0$

If the acid be sufficiently strong to dissolve the first carbide, in addition to the iron, the residue will contain—

Iron	$= c' + c''$
Carbon	$= A + a' + a''$
Hydrogen	$= b$

Finally, when the acid is strong enough to attack also the second and third carbides, the resulting residue will then contain—

Iron . .	$= c''$	or $= 0$
Carbon . .	$= A + A' + a''$	„ $= A + A' + A''$
Hydrogen .	$= b + b'$	„ $= b + b' + b''$

On comparing these theoretical results, it is found that, in accordance with the increased action on the pig iron—

1. The amount of hydrogen in the residue gradually increases from 0 to a maximum.

2. The proportion of iron decreases from a maximum to 0; and that—

3. The amount of carbon also diminishes, though not to 0, since a portion of the carbon in each of the carbides is converted into fixed organic compounds insoluble in acids.

Prost has shown that, unless the acid reaches a certain concentration, the residue remains blackish and dense; but from this concentration onwards its appearance changes—a result necessarily ensuing if the assumption of the presence of different carbides in pig iron be correct. Again, the divergent effects produced by the action of nitric acid on iron carbide are ascribed by de Koninck to the presence of different carbides,

whilst others endeavour to explain them by assuming the presence of semi-combined carbon—an assumption, however, which proves merely that carbon is presumed to occur in at least two forms (in addition to graphite) in iron. In pig iron, however, the carbides undoubtedly form the chief constituent; and, moreover, the above considerations on the carbon compounds would also be applicable to such other metalloids as may be contained in pig iron.

Prost remarks that the amount of hydrogen present in the insoluble residue is such that it cannot be exclusively in combination with the carbon. With regard to this interesting circumstance he promised to make further experiments.

Furthermore, the same worker treated 500 grms. of pig iron with an acid containing 310 grms. of HCl per litre; the washed and dried residue was extracted with absolutely pure ether, and furnished a brown solution which, on evaporation and drying, gave a pappy blackish brown residue, containing—

Carbon	79·70 per cent.
Hydrogen	10·75 ,,
Other elements . . .	9·55 ,,

According to de Koninck, this composition corresponds well to the atomic ratio C_3H_5 or C_5H_8. Prost did not ascertain whether the remaining 9·55 per cent. consisted of oxygen; should, however, this be the case—and in the main it can hardly be otherwise—the atomic ratio corresponding with this composition would agree with the formula $C_{11}H_{18}O$.[1]

Hence the hydrocarbons formed during the solution of iron carbides by hydrochloric acid would subsequently absorb oxygen (probably from the air).

Sulphur, in the form of an organic compound, was found by Prost in the residue from pig iron.

[1] De Koninck erroneously gives $C_{10}H_{16}O_9$.

CHAPTER IV

OPINIONS AND RESEARCHES ON COMBINED CARBON—(*Continuation*)

THE most important investigations on the action of nitric acid on carboniferous iron are those performed by Osmond and Werth.[1]

Comparative examinations by the methods of Eggertz and Boussignault gave—

	Eggertz's Method.	Boussignault's Method.
Ordinary steel . .	0·50 C per cent.	0·492 C per cent.
Hardened steel . .	0·325 „	0·52 „
Steel first hardened, then quickly heated in the forge fire, and cooled in the ashes . .	0·48 „	0·537 „
Wrought steel . .	0·52 „	...

Since hardened steel is soluble in nitric acid without leaving any residue of carbon, and as the coloration of the nitric solution was equal in both cases, the experimenters endeavoured to ascertain whether the deficit in carbon revealed by the Eggertz method had escaped in the form of gas from the solution.

On carefully observing the phenomena occurring during the action of 24 deg. B. nitric acid (25 c.c. per 5 grms. of steel) on one and the same steel in the natural and hardened condition, the following occurrences could be noticed:—

The flasks were set in a water bath at a temperature of 15° C. in order to minimise the increase of tempera-

[1] *Mémorial de l'Artillerie de la Marine*, 1887, p. 227 *et seq.*

ture during the reaction. The iron was the first to dissolve, which it did in about five to six minutes, with a brisk disengagement of gas. At this instant both liquids were almost colourless.

The hardened steel left behind, at the bottom of the vessel, an intensely black substance, which dissolved without any liberation of gas, and that almost immediately when agitated, or in two or three minutes when left at rest, the liquid then turning dark brown. Finally there was left behind a light, brown gelatinous residue, which dissolved only at an extremely slow rate in the cold.

After the iron had dissolved, the sample of natural steel left only a light, black residue, which was otherwise identical with that from the hardened steel, dissolved with equal moderation, and imparted a somewhat faint coloration to the liquid. On the other hand, a large number of blackish brown flakes floated about in the liquid, and gradually collected into a gelatinous pale brown mass, similar to that furnished by hardened steel, but more voluminous.

These flakes, filtered immediately after the hardening carbon had dissolved, and then dried at 100° C., gave—

Carbon	44·59	per cent.
Water	22·50	,,
Iron	8·05	,,
Oxygen and Nitrogen	24·86	,,
	100·00	

This[1] would correspond to $26C + 9H_2O + Fe + 11(O + N)$. Assuming that of the $11(O + N)$ only 1 atom was nitrogen, the other 10 being oxygen, the formula might then be written, $FeC_{26}(H_2O)_9O_8(NO_2)$.

On parting with their iron they become transparent and gelatinous.

[1] H. v. Jüptner, "Kohlenstoffformen im Eisen," Stuttgart, 1896.

On the precipitates being filtered in the cold and then treated anew with 25 c.c. of nitric acid (sp. gr. 1·2) at 100° C., they dissolve without any apparent disengagement of gas, and impart an unequal degree of brown coloration to the liquids; the intensity of this coloration appears to stand in relation with the volume of the precipitate attacked.

If now the first brown liquids (which were separated from the insoluble residues by filtration) be warmed to 100° C., they are both decolorised, with liberation of gas; the solution from the hardened steel, however, bleaches more completely than the other; the evolution of gas appears brisker here and more copious there.

When, instead of immersing the vessel in cold water, the liquid is heated direct to 100° C., the same phenomena appear in the same order, but more quickly. This may be expressed in figures that were quite accidentally discovered among a number of others.

Steel with 0·85 *per cent. of Carbon.*

If we take L_1 to represent the coloured liquids obtained, immediately after the solution of the metallic iron and the hardening carbon, by filtering off the undissolved substance P in the cold; L_2 as the coloured liquids obtained by repeatedly warming the residue at 100° C.[1]; dilute all these solutions to 50 c.c., and compare them with normal steel, we then have—

	Apparent Carbon Content of the Steel— Natural Hardness.		Hardened.	
L_1 (heated for 2 minutes at 100° C.) . .	0·56	1·12 per cent.	0·91	1·17 per cent.
L_2 (heated for 20 minutes at 100° C.) . .	0·56		0·26	

[1] If the heating be effected at 14° C. with 12° B. acid, or at 0° C. with normal 24° B. acid, the liquid L_2 will be greenish.

On comparing the two types of solution again after heating to 100° C. for 45 minutes and 1 hour 45 minutes respectively, we find—

	Apparent Carbon Content of the Steel— Natural Hardness.		Hardened.	
After 45 minutes—				
L_1 (strong escape of gas)	0·28	0·78 per cent.	0·39	0·63 per cent.
L_2 (no „ „)	0·50		0·24	
After 1 hour 45 minutes—				
L_1 (slight escape of gas)	0·24	0·69 „	0·30	0·48 „
L_2 (no „ „)	0·45		0·18	
Under normal conditions the Eggertz test gave		0·81 „		0·41 „

Hence both the natural and the hardened steel immediately after the attack gave perfectly similar colorations (1·12 and 1·17 per cent.). The subsequent heating of L_1 produces the difference; the solution L_2 bleaches regularly and only to a slight extent.

It still remains to show that the decoloration of L_1 is accompanied by a loss of carbon in the gaseous state.

In order to determine the carbon liberated in this manner, the gas escaping with the excess of oxygen during normal solution was passed through an apparatus consisting chiefly of—

1. A condenser.
2. A tube filled with copper turnings and heated to redness, to decompose the oxides of nitrogen.
3. A tube containing copper oxide, also heated to redness, to ensure the complete combustion of the carbon.
4. Drying tubes.
5. A. Liebig's bulb apparatus for the absorption of carbon dioxide.

The average results furnished by a number of experi-

ments with steel containing 0·85 per cent. of carbon, were—

	Steel— Natural Hardness.	Hardened.
Carbon liberated in the gaseous state	0·342 per cent.	0·500 per cent.
Remainder passed into solution .	0·508 „	0·350 „
Total	0·850 „	0·850 „
The coloration of the solution gave .	0·772 „	0·480 „

It is thus seen that the coloration of the solution is apparently proportional to the amount of carbon actually present therein.

If K be taken to represent the coefficient with which the carbon content found has to be multiplied in order to obtain the actual amount of dissolved carbon, we then have—

For steel of natural hardness . .	0·772 K = 0·508
For hardened steel	0·480 K = 0·350

which give for K the values 0·658 and 0·729, thus exhibiting a satisfactory concordance.

The nature of the gas in which the carbon is contained appears to vary, within certain limits, with the conditions of solution.

CO_2 and HCN were detected; but in addition a part of the carbon escaped in a form which was not absorbed by caustic potash (CO or hydrocarbon). This latter portion seems to be characteristic for the hardening carbon.

By treatment with ammoniacal $BaCl_2$ solution (for CO_2) and $AgNO_3$ (for HCN), the actual amounts of CO_2 and HCN obtained during solution were determined as follows:—

Carbon liberated in the Gaseous State as	Steel— Natural Hardness.	Hardened.
CO_2 . . .	0·215 per cent.	0·246 per cent.
HCN . . .	0·050 „	0·044 „
CO or Hydrocarbons (△)	0·077 „	0·210 „
Total . .	0·342	0·500

The presence of gases unabsorbed by caustic potash is highly noteworthy. It was proved by inserting a potash apparatus between the Cu and CuO tubes of the above apparatus. The second Liebig bulb apparatus at the end of the combustion tubes supplements the weight for hardened steel, but not for steel in its natural state of hardness.

These observations fix, by definite phenomena, the difference between hardening and cement carbon.

Stimulated by the foregoing experiments, the present author [1] has worked out a colorimetric method for the determination of hardening and carbide carbon; and as a few of the researches entailed in this process are of interest, they may be repeated here. They were based on the following samples of steel examined by A. Ledebur:—

Constituents.	A.	B.	C.	D.
	Per cent.	Per cent.	Per cent.	Per cent.
Tempering carbon . .	...	0·17	...	...
Carbide carbon . . .	0·64	0·90 } 1·03	{ 0·71	0·38
Hardening carbon . .	0·14	0·13 }	{ 0·22	0·55
Total carbon . . .	0·78	1·20	0·93	0·93
Silicon	0·37	0·79	0·11	0·11
Manganese	0·26	0·40	0·11	0·11
Phosphorus	0·01	0·07	0·03	...

A and B were annealed, C cooled in the ordinary manner, and D hardened in water. The other kinds of steel examined in the course of these researches were cooled in the ordinary way, but their content of hardening and carbide carbon was not determined gravimetrically.

As a rule 0·2 grm. (in some cases more) of the sample was taken, suffused with 10 c.c. of dilute nitric acid (2 vols. of concentrated acid and 3 vols. of water) in a test-tube, which was then set in a vessel of cold water. With frequent shaking, solution was quickly effected. After all liberation of

[1] *Journ. Iron and Steel Inst.*, 1897, vol. i.; *Stahl u. Eisen*, 1897, No. 14.

gas had ceased, the liquid was passed (without washing) through a dry filter "hardened" with nitric acid, and 2 c.c. of the filtrate taken in a measuring tube for comparison with a similarly treated solution of normal steel. When the steel under examination contains only small quantities of hardening carbon, the solution assumes a greenish colour, which hinders comparison. For exact determinations in such cases it is therefore necessary to use a normal steel that also furnishes greenish solutions, or else a larger quantity of substance is weighed out. By this method the following average values were obtained:—

Sample.	Hardening Carbon.		
	Gravimetric.	Colorimetric.	Difference.
A	0·140	0·14	0·000
B	0·128	0·13	− 0·002
C	0·218	0·22	− 0·002

The behaviour of the above solutions on prolonged standing and on warming to 80° C. was then examined, and in both cases a gradual bleaching was observed. In the first case (twenty-four hours standing in the cold) the loss of hardening carbon is very slight, as the following figures will show:—

Sample.	Loss of Hardening Carbon.
A . . .	0·14 × 0·167 = 0·02338 per cent.
B . . .	0·13 × 0·219 = 0·02847 „
C . . .	0·22 × 0·069 = 0·02518 „
F . . .	0·09 × 0·276 = 0·02484 „

so that no appreciable error results from leaving the solutions to stand for several hours. When it is remembered that the amount of this loss is influenced to a considerable extent by an alteration of 0·1 c.c. in the volume of the compared liquids,

it becomes probable that, for equal periods of time, the same depends solely on the superficial area of the solutions in question, and is therefore attributable to a process of oxidation under the influence of atmospheric oxygen, or to volatilisation of the carbon compounds.

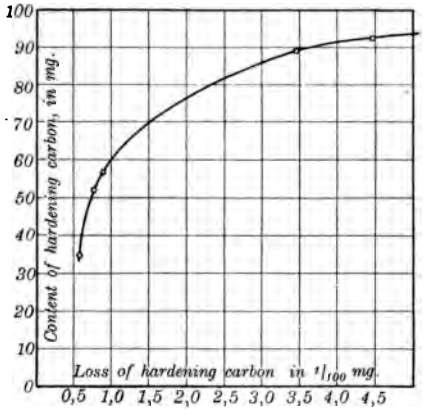


FIG. 81.

The case is different when the solutions are heated to 80° C., the loss of carbon then rapidly increasing with the amount of hardening carbon present, as the following figures will show:—

Sample.	Amount of Hardening Carbon present in mgrms.	After 30 Minutes' Heating at 80° C.	
		Decrease of Coloration in per cent.	Loss of Hardening Carbon in mgrms.
E	0·0355	17·3	0·00614
B	0·0520	13·5	0·00703
A	0·0560	19·3	0·01079
C	0·0880	38·9	0·03426
F	0·0920	48·7	0·04476

This is shown still more clearly by the graphical representation given in Fig. 81.

The progress of the colour change in relation to the duration of heating is given in the subjoined table :—

No.	Sample.	Volume of Hardening Carbon Solution in c.c., compared with Normal Solution after Heating to 80° C. for—					Colour Depth of the Solution in per cent. after Heating to 80° C. for—				
		0 Min.	15 Min.	30 Min.	45 Min.	60 Min.	0 Min.	15 Min.	30 Min.	45 Min.	60 Min.
1	A[1]	3·0	2·8	2·6	2·3	2·1	100·0	93·3	86;7	76·7	70·0
2	B[1]	3·2	2·9	2·9	2·2	2·1	100·0	90·6	90·6	66·7	65·6
3	C[1]	7·3[2]	5·5	4·9	4·9	4·6	100·0[2]	75·3	67·1	67·1	63·0
4	F[1]	2·9	2·6	2·4	2·2	2·3	100·0	89·6	82·7	75·8	79·3
5	A	3·9	...	...	...	3·2	100·0	...	...	...	82·1
6	B	3·8	...	...	...	3·0	100·0	...	...	...	78·9
7	C	6·3	...	...	...	5·5	100·0	...	...	...	87·3
8	A	3·9	..	2·0	...	...	100·0	...	51·3	...	...
9	B	3·5	...	1·9	...	...	100·0	...	54·3	...	...
10	C	5·2	...	3·0	...	...	100·0	...	57·7	...	...
11	F	5·5	...	2·9	...	...	100·0	...	52·7	...	...
12	A	4·2	...	2·2	...	...	100·0	...	52·4	...	...
13	B	3·5	...	2·3	...	...	100·0	...	65·7	...	...
14	C	5·5	...	3·2	...	...	100·0	...	58·2	...	...
15	F	6·2	...	3·1	...	...	100·0	...	50·0	...	...

Another, and in some cases preferable, method of determining the hardening carbon is by dissolving the steel as

Sample.	Series of Experiments.		
	1	2	3
	1 c.c. of Solution corresponds to mgrms. of Hardened Carbon.		
A	0·01914	0·02800	0·02545
B	0·01793	0·02737	0·02261
C	0·01796	0·02933	0·02750
Mean . .	0·01834	0·02823	0·02519

[1] The initial temperature was below 70° C. [2] Turbid, but cleared on heating.

before in cold dilute nitric acid, filtering the solution through a dry hardened filter, heating an aliquot part to 80° C. on the water bath, and then comparing the depth of colour. This method furnished the above results (after thirty minutes at 80° C.).

With regard to the estimation of the carbide carbon, the next step was to dissolve in dilute acid at 80° C. the residue on the hardened filter from the preceding operation. As before, the metal was dissolved in 10 c.c. of cold dilute nitric acid, the residue collected on a dry hardened filter, the filtrate employed for the determination of the hardening carbon, the filter well washed with distilled water, and transferred with its contents to a test-tube, there suffused with 10 c.c. of dilute nitric acid, and afterwards warmed at 80° C. on the water bath until the residue was completely dissolved. After the filter fibres had settled down, 2 c.c. of the clear solution were placed in a measuring tube and compared with the normal solution. The following are some average values obtained by this means:—

Sample.	Carbide Carbon, per cent.		
	Gravimetric.	Colorimetric.	Difference.
A. . .	0·64	0·65	+0·01
B. . .	0·90	0·95	+0·05
C. . .	0·71	0·70	−0·01

As the foregoing figures show, the differences furnished by this method are greater than occur in the estimation of hardening carbon, which may be due in part to the loss of carbon in filtering, but chiefly to the fact that, in dissolving the steel at 80° C., various amounts of the solvent are volatilised according to the time required for the operation and the superficial area of the liquid, the result being that the amount

of liquid pipetted off does not exactly correspond with that taken into calculation. Moreover, small particles of the carbide may remain unnoticed in the fibres of the filter paper, thus leading to a deficit of carbide carbon in the solution. In order to minimise this difficulty as much as possible, and to simplify the work, the following (second) method for the simultaneous determination of hardening and carbide carbon was devised:—

To determine the hardening carbon, 0·2 grm. of steel is dissolved in dilute nitric acid (2 : 3) in the cold, *i.e.* by setting the vessel in cold water. The solution is shaken up frequently, and, when the evolution of gas has apparently ceased, is well mixed up and filtered through a dry hardened filter without washing. Two c.c. of the filtrate are taken for the determination of the hardening carbon, by direct comparison with the standard solution, whilst another 2 c.c. are set aside for the present.

Meanwhile, for the estimation of the carbide carbon, 0·4 grm. of the sample is weighed out, treated with 10 c.c. of the aforesaid dilute nitric acid and the 2 c.c. of hardening-carbon solution just mentioned, and warmed to 50° C. on the water bath. As soon as complete solution is obtained, both series of solutions are taken from the water bath and compared with the same standard solution. The compared volume of the hardening-carbon solution warmed to 80° C. is deducted from the compared volume of the solution of the total carbon, thus leaving a volume of solution corresponding to the carbide carbon, from which the percentage of carbide carbon can be easily calculated.

For the comparison it is convenient to employ an unchangeable empirical standard solution, consisting of a slightly acidified solution of Fe_2Cl_6 and $CoCl_2$; the addition of hydrochloric acid must be made with care, since otherwise the colour of the solution may become too green. If a high

degree of accuracy be desired, it is advisable to employ, for comparison, two standard solutions differing but slightly in shade.

Should the measuring tubes used for the comparison not be exactly equal in width, as may be ascertained by comparing the interval between the graduations, a correction (by volume) can easily be made when it is remembered that the depth of colour in any solution is directly proportional to the thickness of the stratum of liquid, and hence in inverse proportion [1] to the root of the heights of equal volumes of liquid. The colorimetric determination of hardening and carbide carbon is an easy, quick, and satisfactory method. It is nevertheless attended with certain difficulties, which must be mentioned. One of the chief sources of error is the readiness with which the carbide is attacked by acids, in consequence of which it is somewhat difficult to obtain standard samples of steel with an accurately known percentage of hardening and carbide carbon.

Furthermore, the solution of carbide carbon in dilute nitric acid is not perfectly stable. The following table shows the loss of carbon in these solutions (or, more correctly, the degree of decoloration) after prolonged standing, expressed in milligrams :—

Sample.	Carbide Carbon per 1 c.c. mgrms.	Loss of Carbon in mgrms., after Standing—			
		Twenty Hours.	Twenty-four Hours.	Twenty-six Hours.	Forty-five Hours.
A .	0·262	...	0·014	...	...
,, .	0·360	0·015	...	0·013 (0·028)	0·007 (0·035)
B .	0·380	...	...	0·000	...
,, .	0·536	0·044	...	0·052 (0·096)	0·020 (0·116)
C .	0·049	...	0·015	...	...

As the above figures show, this alteration is, however, so

[1] For examples see the references already cited.

slight that no appreciable error is produced, even if the liquid be left to stand for several hours.

The solutions of the hardening carbon, however, behave in a very different manner. It has already been stated that these solutions, when warmed, are more strongly bleached in proportion as their content of hardening carbon is greater. Moreover, the colouring power of the original solution appears to differ according to the variations in the carbon content, even in the case of one and the same steel in a hardened and in the annealed state. Thus the samples C (natural hardness) and D (the same steel hardened in water) gave the values—

HARDENING CARBON.

Sample.	C			D.		
No.	Colorimetric, per cent.	Gravimetric, per cent.	Difference, per cent.	Colorimetric, per cent.	Gravimetric, per cent.	Difference, per cent.
1	0·2360	0·22	+0·0160	0·3730	0·55	−0·1770
2	0·2250	0·22	+0·0050	0·3940		−0·1560
3	...	...	...	0·3677		−0·1823
4	...	...	...	0·3730		−0·1770
5	...	...	...	0·3568		−0·1932
Mean	0·2310	0·22	+0·0110	0·3729	0·55	−0·1771
CARBIDE CARBON.						
1	0·7102	0·71	+0·0002	0·4345	0·38	+0·0548
2	...	...	...	0·4056		+0·0256
3	...	...	..	0·4042		+0·0242
Mean	0·7102	0·71	+0·0002	0·4147	0·38	+0·0347

This shows the necessity—in the estimation both of the hardening carbon and the total carbon, by the ordinary

Eggertz method—of using standard steel containing as nearly as possible similar percentages of both total and hardening carbon.

The matter in question is a loss of carbon occurring in the Eggertz test, to which attention was first called by H. J. Howe,[1] who referred to it as "missing carbon," and with regard to which T. W. Hogg[2] published an interesting research, which must now be dealt with at length.

When nitric acid of sp. gr. 1·2 is used, the colorimetric test furnishes results which are classified by T. W. Hogg as follows:—

Condition of the Carbon in the Steel.	Effect of Cold Acid.
(*a*) Amorphous carbon . .	Black, insoluble.
(*b*) Normal carbide . . .	Black, magnetic, insoluble.
(*c*) Dissolved carbide . .	Brown, insoluble nitro-compound.
(*d*) Unknown carbide . .	Either immediately decomposed, with evolution of CO_2, or forming a colourless compound.

(*a*) (Amorphous carbon), which is also left unattacked by hot acid, can only appear in steels rich in carbon and low in manganese;[3] (*b*) is decomposed by hot nitric acid, both the iron and a brown nitro-compound passing into solution; (*c*) is dissolved even by cold acid, a brown nitro-compound being formed; finally, Hogg regards the condition (*d*) as identical with the so-called hardening carbon.[4]

[1] *Journ. Iron and Steel Inst.*, 1896, vol. i. p. 170.

[2] *Journ. Iron and Steel Inst.*, 1896, vol. ii. p. 179.

[3] Tempering carbon.

[4] According to Osmond and Werth, hardening carbon is that form of the element which is dissolved by cold dilute nitric acid, and therefore comprises the forms (*c*) and (*d*) of Hogg. Moreover, it is by no means certain that there exists a definite form of carbon behaving like Hogg's form (*d*); it is quite possible that the different forms of carbon should possess unequal colouring properties.

It is thus evident that Hogg, like the author[1] and others, was led to assume the existence in steel of a hitherto unknown form of carbon.

Hogg gives the following table relating to steels of increasing carbon content, and with 0·4 to 0·6 per cent. of manganese, hardened in cold water:—

Actual Carbon Content determined by Combustion, per cent.	Colorimetrically estimated Carbon in Hardened Steel, per cent.	C-Difference "Missing Carbon," per cent.	C-Difference in percentage of Total Carbon, per cent.
0·10	0·06	0·04	40·00
0·14	0·10	0·04	28·57
0·21	0·10	0·11	47·62
0·25	0·13	0·12	48·00
0·30	0·17	0·13	43·33
0·35	0·17	0·18	51·43
0·39	0·23	0·16	41·02
0·45	0·25	0·20	44·44
0·50	0·28	0·22	44·00
0·62	0·41	0·21	33·87
0·70	0·35	0·35	50·00
0·75	0·32	0·43	57·33
0·84	0·35	0·49	58·33
0·92	0·41	0·51	55·43
1·00	0·50	0·50	50·00
1·25	0·74	0·51	40·80
1·50	1·10	0·40	26·66
1·64	1·33	0·31	18·90
1·70	1·35	0·35	20·58
2·40	2·10	0·30	12·50
3·10	2·82	0·28	9·03
6·50	6·50	0·00	0·00

The alloy, with 3·1 per cent., contained merely traces of amorphous carbon (tempering carbon), manganese, and silicon.

The alloy with 6·50 per cent. is a ferromanganese; in this case rapid cooling does not appear to exert any influence on the carbon.

It is certainly very remarkable that the Eggertz test

[1] "Kohlenstoffformen im Eisen" (Forms of carbon in Iron), Dr. Ahrens' Collection of Chem.-Techn. Lectures (Sammlung chem.-techn. Vorträge), vol. i. p. 453.

should have given a maximum of loss in the case of a hardened steel with about 0·88 per cent. of carbon, *i.e.* a percentage corresponding with Professor Arnold's saturation point (with 0·89 per cent. C).[1]

Basing on Arnold's theory, E. H. Saniter put forward the following calculation in the discussion on Hogg's researches:—

It follows from Hogg's table that 0·89 per cent. of carbon in hardened steel—*i.e.* 100 per cent. of Arnold's sub-carbide ($Fe_{24}C$)—gives the same coloration as 0·385 per cent. of carbon[2] as normal carbide (Fe_3C). If now, in steel containing less than 0·89 per cent. of carbon, this latter be present solely as sub-carbide, whereas in those with a higher percentage of carbon it occurs in alternating amounts of $Fe_{24}C$ and Fe_3C (in accordance with the excess of carbon beyond the saturation point), the intimate composition of the quenched steel will work out as follows:[3]—

For quenched steel with 1·7 per cent. of carbon the saturation point will, for example, be reduced to 0·76 per cent. of carbon, *i.e.* not more than 0·76 per cent. can exist as $Fe_{24}C$, the rest being then necessarily present as Fe_3C.

For hardened steel with less than 0·89 per cent. of carbon, the result of the Eggertz test works out according to the equation—

$$\frac{\text{Total carbon} \times 0{\cdot}385}{0{\cdot}89}$$

For quenched steel with more than 0·89 per cent. of carbon, it was assumed that the carbon of the carbide Fe_3C

[1] *Minutes of Proceedings of the Inst. of Civil Eng.*, vol. cxxiii. p. 127–162.

[2] Calculated proportionately from the values for 0·84 and 0·92 per cent. of C.

[3] Saniter's conclusions appear somewhat hazardous.

gave the full colour value (1), whilst that of the sub-carbide calculates out as—

$$\frac{\text{Sub-carbide} \times 0{\cdot}385}{0{\cdot}89}.$$

By the aid of this method, and on the basis of Hogg's reports, Saniter calculated out the following table:—

Calculated Percentage Composition of the Hardened Steel.			Percentage of Total Carbon (Hogg).	Percentage of Carbon found by Colorimetric Examination.		Difference, per cent.
Fe.	Fe_3C.	$Fe_{24}C$.		Found by Hogg.	Cal. by Saniter.	
88·7	...	11·3	0·10	0·06	0·043	−0·017
84·2	...	15·8	0·14	0·10	0·06	−0·04
76·3	...	23·7	0·21	0·10	0·09	−0·01
71·8	...	28·2	0·25	0·13	0·11	−0·02
66·1	...	33·9	0·30	0·17	0·13	−0·04
60·5	...	39·5	0·35	0·17	0·15	−0·02
55·9	...	44·1	0·39	0·23	0·17	−0·06
49·2	...	50·8	0·45	0·25	0·19	−0·06
43·5	...	56·5	0·50	0·28	0·22	−0·06
29·9	...	70·1	0·62	0·41	0·27	−0·14
20·9	...	79·1	0·70	0·35	0·30	−0·05
15·3	...	84·7	0·75	0·32	0·32	0
5·1	...	94·9	0·84	0·35	0·36	+0·01
...	0·5	99·5	0·92	0·51	0·41	0
...	2·0	98·0	1·00	0·50	0·50	0
...	6·35	93·35	1·25	0·74	0·78	+0·04
...	10·7	89·3	1·50	1·10	0·98	−0·12
...	13·05	86·95	1·64	1·33	1·20	−0·13
...	14·1	85·9	1·70	1·35	1·27	−0·08
...	26·25	73·75	2·40	2·10	2·13	+0·03
...	38·4	61·6	3·10	2·82	2·79	−0·03

The agreement between the calculated carbon content and that found by direct colorimetric examination is certainly remarkable.

Albert Sauveur states that the ratio between the colorimetric carbon deterioration and the percentage of total carbon in hardened steel is almost constant, up to about 1 per cent., with only two exceptions. If, however, the carbon percentage exceed 1 per cent., the colorimetric loss of carbon rapidly decreases. To explain this, he draws into considera-

tion the microscopic structure of hardened steel with different percentages of carbon. It is known that—

1. The carbon of hardened steel appears as carbide carbon (in cementite) and as hardening carbon (in martensite), and

2. That the loss of carbon occurring in the examination of hardened steel by the Eggertz test is confined entirely to the hardening carbon.

Sauveur calculated the following table in the subjoined manner:—

If c be the total carbon in the steel, x the percentage of martensite, and y that of the cementite, we have—

$$x + y = 100$$

and, since the martensite contains 0·9 per cent., whilst the cementite contains 6·67 per cent. of carbon—

$$\frac{0{\cdot}90x}{100} + \frac{6{\cdot}67y}{100} = c.$$

These two equations give—

$$y = \frac{100c - 90}{577}$$

and therefore the percentage of cement carbon is—

$$\frac{(100c - 90)\ 6{\cdot}67}{577}$$

whilst the rest is martensite carbon.

In the following table the columns 3 and 4 give the percentage of martensite and cementite carbon in the steel, whilst the two final columns show the waste of carbon produced in the Eggertz test, expressed in percentages of the total carbon and martensite carbon respectively.

[TABLE

Total Carbon (Hogg).	Metallographic Composition.		Martensite Carbon.	Cementite Carbon.	Decrease of Carbon.	Decrease of Carbon in per cent. of–	
	Martensite.	Cementite.				Total Carbon.	Martensite Carbon.
per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
0·10	85M + 15F	0	0·10	0	0·04	40	40
0·14			0·14		0·04	29	29
0·21			0·21		0·10	48	48
0·25			0·25		0·12	48	48
0·30			0·30		0·13	43	43
0·35			0·35		0·18	51	51
0·39	100	0	0·39	0	0·16	41	41
0·45			0·45		0·20	44	44
0·50			0·50		0·22	44	44
0·62			0·62		0·21	34	34
0·70			0·70		0·35	50	50
0·75			0·75		0·43	57	57
0·84			0·84		0·49	58	58
0·92	99·65	0·35	0·90	0·02	0·51	55	57
1·00	98	2	0·89	0·11	0·50	50	56
1·25	94	6	0·85	0·40	0·51	41	60
1·50	90	10	0·81	0·69	0·40	27	49
1·64	87	13	0·78	0·86	0·31	19	40
1·70	86	14	0·77	0·93	0·35	21	45
2·40	74	26	0·67	1·73	0·30	12	45
3·10	62	38	0·56	2·54	0·28	9	50
6·50	3	97	0·03	6·47	0·00	...	...
						Mean	47

The above decrease of carbon, therefore, amounts to 47 per cent. of the martensite carbon present, or, apart from the abnormal values, 29 and 34 per cent., 49 per cent.

Thus about one half the martensite carbon escapes detection by the colorimetric method. This coincides precisely with the carbon determinations made by Howe,[1] who found a loss of 45 per cent. in the case of steel with 0·21 per cent. of carbon after quenching above the critical point; it also agrees with the figures of Osmond and Werth, according to whom the loss of carbon in a steel with 0·90 per cent. of C amounted to 47 and 51 per cent. From this Sauveur concludes that the diminution of carbon stands

[1] "Hardening of Steel," *Journ. Iron and Steel Inst.*, 1895, ii. p. 258.

in a constant relation to the percentage of carbon in the martensite.

Howe's treatise, already referred to, is of special interest, when, as in our case, it is a question of determining the different forms of combined carbon in general. With steel with 0·21 per cent. of C he obtained the following figures:—

No.	Hardening Temperature, ° C.		Decrease of Carbon, per cent.	Percentage Metallographic Composition.		
				Martensite.	Pearlite.	Ferrite.
6	880	Above Ar_2	0·092	100		0
7	836		0·095			
4	797		0·102			
16	761		0·082			
15	733		0·095			
			Mean = 0·094			
12	714	Commencement of Ar_2	0·102	97·20	0	2·80
18	713		0·093	86·00		14·00
9	698	Middle of Ar_2	0·096	70·20		29·80
5	652	Between Ar_2 and Ar_1	0·100	35·20		64·80
14	650		0·084	30·80		69·20
21	633		0·084	32·00		68·00
10	626		0·084	31·50		68·50
22	620	Commencement of Ar_1	0·091	30·00	1·60	68·40
11	600	End of Ar_1	0·034	4·00	17·50	78·50
3	590		0·047	2·00	22·20	75·80
8	575	Below Ar_1	0·029	0	21·10	78·90
9	532		0·005		23·20	76·80
13	512		0·018		23·00	77·00
17	340		0·000		22·60	77·40
20	263		0·000		24·80	75·20
23	20		0·008		23·60	76·40

On calculating from these data the decrease of carbon, in percentages of the total carbon (which in this case = martensite or pearlite carbon), we obtain—

No.		Martensite, per cent.	Pearlite, per cent.	Decrease of Carbon in per cent. of Total Carbon.	Mean.	
6	Above Ar_2	100	0	43·9	44·5	45·1
7				45·2		
4				48·6		
16				39·5		
15				45·2		
12	Commencement of Ar_2	97·20	0	48·6	46·5	
18		86·00		44·3		
9	Middle of Ar_2	70·20	0	45·7	45·7	
5	Between Ar_2 and Ar_1	35·20	0	47·6	41·9	
14		30·80		40·0		
21		32·00		40·0		
10		31·50		40·0		
22	Commencement of Ar_1	30·00	1·60	43·3	43·3	27·3
11	End of Ar_1	4·00	17·50	16·2	19·3	
3		2·00	22·20	22·4		
8	Below Ar_1	0	21·10	13·8	4·8	
19			23·20	2·4		
13			23·00	8·6		
17			22·60	0·0		
20			24·80	0·0		
23			23·60	3·8		

Reverting once more to the previously cited work of the author, we find the value of 1 c.c. of the compared solutions of total carbon—

In the case of sample	A	0·78 : 15·30 = 0·051	per cent.	C.
,, ,,	B	1·03 : 21·29 = 0·0484	,,	,,
,, ,,	C	0·93 : 18·44 = 0·0504	,,	,,
,, ,,	F	1·414 : 26·32 = 0·0537	,,	,,
	Mean		0·0509 per cent.	C.

On the other hand, the value of 1 c.c. of the cold-prepared solution of hardening carbon in the same examples averages 0·059 per cent. of hardening carbon, and thus we obtain the average decrease of carbon in the case of the hardening carbon as—

$$\frac{0{\cdot}059 - 0{\cdot}051}{0{\cdot}051} = 15{\cdot}7 \text{ per cent.}$$

On comparing the relative colouring power of the solutions

of hardening and carbide coal, in the same examples, and in sample D, and setting down that of the carbide as = 100, we obtain—

Sample A (annealed) . .	78·46	mean 78·17
„ B „ . .	77·87	
„ C (natural hardness) .	83·66	
„ D (hardened in water .	52·55	

Hence we have—

Colouring Power of Solution from—	Howe.	Osmond and Werth.		Sauveur.	Jüptner.	
Carbide carbon . . .	...	104	100	...	108	100
Total carbon . . .	100	100	96	100	100	92·7
Hardening carbon in annealed steel . . .	...	88	85	...	84	78
Hardening carbon in hardened steel . . .	55	51	65	51	53	52

i.e. a concordance between the various independent experiments, that is the more remarkable when it is remembered that they were based on different normal steels (*i.e.* in different conditions of hardness).

It may therefore be considered as proved that the different forms of carbon in nitric solution have different colouring powers. The carbide carbon is the strongest in this particular, the hardening carbon being weaker; though with regard to the latter a distinction must be drawn between two varieties of different colouring power. Of these, the hardening carbon from annealed steel is stronger than that from hardened steel; the former variety occurs in pearlite, the latter in martensite.

If we arrange these forms of carbon in accordance with their colouring power, we have—

Kind of Carbon.	Colouring Power.
Hardening carbon in Martensite .	52 = 2·08 or nearly 2
„ „ Pearlite .	78 = 3·10 „ 3
Carbide carbon in Pearlite . .	100 = 4·00 „ 4

Consequently, in view of their chemical behaviour, we may apply to these three forms of carbon the simple names, bi-, tri-, and tetra-carbon, their occurrence being, moreover, as follows:—

In Martensite (chiefly, if not solely)	bi-carbon.
Free cementite	bi-, tri-, and tetra-carbon.
Pearlite	tri- and tetra-carbon.

CHAPTER V

OPINIONS AND RESEARCHES ON COMBINED CARBON—(*Conclusion*)

TURNING to the matter of researches mainly concerned with the gaseous products obtained when iron-carbon alloys are dissolved in acids, mention must first be made of the labours of Helge Bäckström and Gunnar Paijkul,[1] who determined the amount and carbon percentage of the gases liberated in dissolving different kinds of iron in acids. The process of solution being effected without access of air, these workers attempted at the same time to determine the iron content in the resulting solutions, by titration with permanganate. The results obtained, however, were fluctuating and generally too high, whence it was concluded that a portion of the carbon is dissolved in the liquid in the form of some organic compound exhibiting a peculiar odour.

The results obtained are collected in the subjoined table on next page.

From these data it follows that—

1. The carbon liberated as gaseous hydrocarbon is not in proportion to the combined carbon present;

2. None of the kinds of iron examined gave off either the whole or a proportional part of the combined carbon as gas;

[1] Fresenius, *Zeitzs. f. analyt. Chemie*, 1887, p. 683.

3. Hydrochloric acid gives a larger volume of gas, and one richer in carbon than sulphuric acid of the same relative strength (1 : 25);

4. The volume of gas liberated[1] is not in proportion to the percentage of chemically combined carbon present.

Total Carbon in Iron, per cent.	Kind of Iron.	C.c. of Gas from 1 grm. of Iron.	Carbon in Iron, per cent.
0·00	Pure iron (atomic weight, 55·91) evolves	399·6	...
0·11	Eggertz's normal wire	398·7	...
0·20	Iron wire	396·9	...
0·26	Eggertz's normal wire	392·5	0·180
		393·6	0·165
0·50	Iron wire from Bofors	378·5	0·346
0·60	,, ,, ,,	386·3	0·356
0·60	Iron	391·3	...
1·00	Steel wire from Bofors	356·0	0·242
1·00	Bessemer steel with 0·13 per cent. of tempering carbon	383·2	0·776
		380·2	0·645
1·30	Eggertz's normal wire	353·3	0·492
3·28	White pig iron with 0·41 per cent. of graphite	297·8	1·94
		298·4	2·12
3·80	Grey pig iron with 3·45 per cent. of graphite	383·3	...
3·87	White pig iron dissolved in sulphuric acid	295·7	2·245
		290·8	2·276
		282·8	2·235
	,, ,, ,, HCl	309·5	2·546
		311·1	2·552
3·90	Grey pig iron with 3·55 per cent. graphite	372·0	...
4·24	White pig iron	296·3	2·806
6·37	Ferromanganese with 84·30 per cent. of Mn, 7·72 per cent. Fe, no graphite	287·5	3·80

The influence of hardening on the gaseous products evolved is expressed in the table on next page.

Hence hardened steel furnishes a larger volume and a more carbonaceous gas than unhardened; nevertheless, even here the differences between the volume of gas liberated and the amount of carbon are by no means proportional.

[1] Also the difference between the volume of gas actually found and that calculated from the iron content.

The earliest investigations on the nature of the evolved gases date as far back as 1864. Hahn[1] obtained divers hydrocarbons from different sorts of iron; some of these were gaseous, and belonged to the olefine series (C_nH_{2n}); another portion, also gaseous, belonged to the paraffin series (C_nH_{2n+2});

Analysis.	Kind of Iron.	Percentage of Carbon.	Unhardened.		Hardened.	
			C.c. of Gas from 1 grm. Iron.	Grms. C in Gas from 1 grm. Iron.	C.c. in Gas from 1 grm. Iron.	Grms. C in Gas from 1 grm. Iron.
I. 1	Iron wire from Bofors .	0·30	393·8	0·0009	398·5	0·0018
2	,, ,, ,, .	0·30	393·8	0·0013	398·5	0·0018
II. 1	,, ,, ,, .	0·50	384·9	0·0015	397·5	0·0035
2	,, ,, ,, .	0·50	...	...	397·5	0·0034
3	Iron wire from Bofors, cold hammered	0·50	380·4	0·0012	...	...
4	Iron wire from Bofors, cold hammered	0·50	380·4	0·0013	...	...
III. 1	Iron wire from Bofors .	0·60	386·3	0·0034	395·0	0·0045
2	,, ,, ,, .	0·60	386·3	0·0038	395·0	0·0044
IV. 1	,, ,, ,, .	1·00	356·0	0·0025	386·1	0·0088
2	,, ,, ,, .	1·00	356·0	0·0023	386·1	0·0077
3	,, ,, ,, .	1·00	354·0	0·0016	386·1	0·0088
4	,, ,, ,, .	1·00	355·6	...	...	...
5	Iron wire from Bofors, cold hammered	1·00	345·1	0·0012	...	...
6	Iron wire from Bofors, cold hammered	1·00	345·4	0·0013	...	...
V. 1	Eggertz's normal wire .	1·30	359·2	0·0051	384·4	0·0083
2	,, ,, ,, .	1·30	353·3	...	384·3	...
3	,, ,, ,, .	1·30	351·2	0·0084	...	...

whilst another consisted of unknown liquid hydrocarbons. In 1887 Cloëz[2] dissolved manganiferous white pig iron, converted the olefine hydrocarbons in the evolved gases into the di-bromine derivatives ($C_nH_{2n} + Br_2 = C_nH_{2n}Br_2$) by absorption in bromine, and detected a part of the unabsorbed gases as paraffins liquid of low boiling point ($C_{12}H_{26}$ in particular), a residue of liquid hydrocarbons being left unidentified. Both

[1] Liebig's *Chem. Ann.*, 129, p. 57.
[2] *Compt. rend.*, 85, x. 3.

Hahn and Cloëz qualitatively proved the presence of the olefines—

Ethylene	C_2H_4
Propylene	C_3H_6
Butylene	C_4H_8
Pentylene	C_5H_{10}
Di-butylene	C_8H_{14}

and Cloëz identified the paraffins—

Decane	$C_{10}H_{22}$
Monodecane (Undecane)	$C_{11}H_{24}$
Dodecane	$C_{12}H_{26}$ (preponderating)
Tridecane	$C_{13}H_{28}$
Tetradecane	$C_{14}H_{30}$
Pentadecane	$C_{15}H_{32}$
Hexadecane	$C_{16}H_{34}$.

Whereas the labours of these workers were chiefly of a qualitative character, E. W. Campbell[1] attempted to carry on the investigation in a strictly quantitative manner.

The method employed was as follows:—The steel was dissolved in hydrochloric acid, the liberated gases being passed through bromine, in order to convert the unsaturated hydrocarbons into their di-bromine derivatives ($C_nH_{2n}Br_2$), whilst the unabsorbed portion was measured, and the carbon contained in the gaseous paraffins therein was determined by the explosion method and by measuring the resulting CO_2. The di-bromine derivatives were purified, dried, weighed, analysed, and subjected to fractional distillation for the identification of the individual constituents of the mixture. Although the fractional distillation test revealed the presence of ethylene, propylene,

[1] *Trans. Amer. Inst. Ming. Eng.*, Feb. 1897; *Journ. Iron and Steel Inst.*, 1899, vol. ii.

butylene, pentylene, and hexylene di-bromide, as well as of di-butylene tetra-bromide, subsequent investigations showed that the latter body is formed, during distillation, by the polymerisation of butylene di-bromide, and is not present — in any appreciable amount at least — in the original derivatives. However, although all the derivatives, from ethylene di-bromide to hexylene di-bromide, could be detected qualitatively, their separation in a quantitative manner by fractional distillation *in vacuo* could not be effected with sufficient precision. Consequently, for the time being at least, Campbell had to content himself with calculating from the bromine content of the derivatives the mean number of carbon atoms in the molecule.

The results of his examination of several samples of steel are given below :—

Sple.	Thermal Treatment of the Samples.	Carbon Content in the Steel, per cent.	Percentage of Carbon in— (of the Total Carbon.)			Bromine Content in the Derivatives, per cent.	Calculated number of C. atoms in the mol. of Br Derivative.
			the Derivatives	the Gaseous Paraffins	the unknown Compounds		
F	Annealed .	0·55	37·1	33·6	29·3	·72·56	4·32
F	Hardened and annealed	0·55	25·0	...	...	75·65	3·67
C	Annealed .	1·14	43·4	37·9	18·7	73·85	4·05
C	Hardened .	1·14	29·0	48·6	22·4	77·61	3·31
D	Annealed .	1·28	31·0	44·3	24·7	77·80	3·26
...	Pure carbide from D (annealed)	6·64	35·3	25·2	39·5	...	4·41

The number of carbon atoms in the molecule of the derivative obtained from the pure carbide was deduced from the results of the gas analysis by dividing the volume of CO_2, formed by the explosion of the olefines, by the initial volume of the olefines.

From the foregoing data Campbell concluded—

1. That the mean number of carbon atoms in the molecule of derivatives from annealed steel varies inversely with the carbon content;

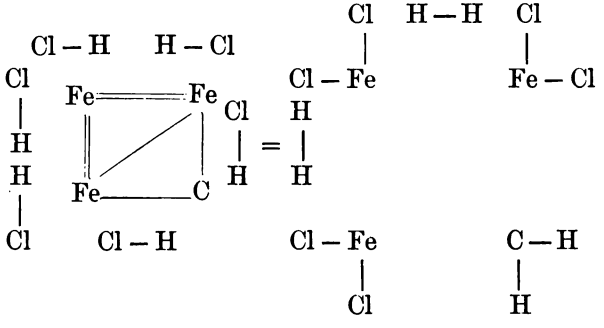
2. That the amount of the gaseous paraffins liberated (probably methane, CH_4, or ethane, C_2H_6) increases with the carbon content;

3. That, in one and the same steel, hardening seems to diminish the number of carbon atoms in the molecule of the derivative, whilst on the other hand the amount of carbon in the liberated gaseous paraffins is increased;

4. That, from the carbon content of the above samples of steel, it follows that "F, annealed" must consist of pearlite and ferrite, "C, annealed" and "D, annealed," on the other hand, of pearlite, with increasing quantities of cementite. The number of carbon atoms in the molecule of derivatives from "F, annealed," and in the pure carbide isolated from the "D, annealed," is nearly identical (4·32 and 4·41). Since the number of carbon atoms from "D, annealed" is far smaller than in the free carbide isolated therefrom, the free cementite must yield derivatives with a smaller atomic proportion of carbon than the isolated carbon, in order to furnish the mean 3·26.

From these researches Campbell rightly concludes that various carbides, with different molecular weights, must exist in steel. All previous investigations gave the empirical formula Fe_3C for the carbide of annealed steel; consequently the only course open is to assume that iron forms with carbon a series of compounds (to which Campbell gives the appropriate name "ferrocarbons"), exhibiting the empirical formula $(CFe_3)_n$, or, more correctly, C_nFe_{3n}. These compounds constitute a homologous series, the members of which may be regarded as derivatives of the olefine series, in which each pair of hydrogen atoms is replaced by the di-valent group of

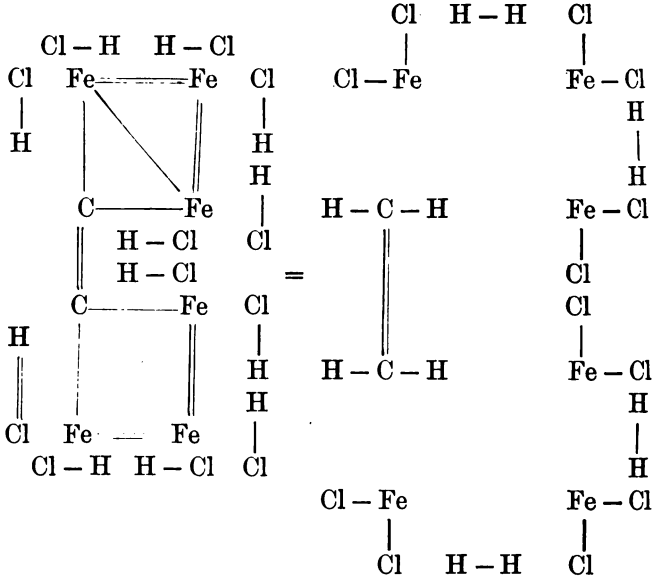
atoms $Fe\begin{cases}Fe—\\Fe—\end{cases}$.[1] On solution in hydrochloric acid, these hydrocarbons furnish hydrogen and the corresponding olefines as primary decomposition products. Whether a ferrocarbon of such simple composition as $Fe\begin{cases}Fe\\Fe\end{cases}C$ (the first member of this homologous series) actually exists, is unknown, and will probably remain so, since the initial products of solution in hydrochloric acid would be—



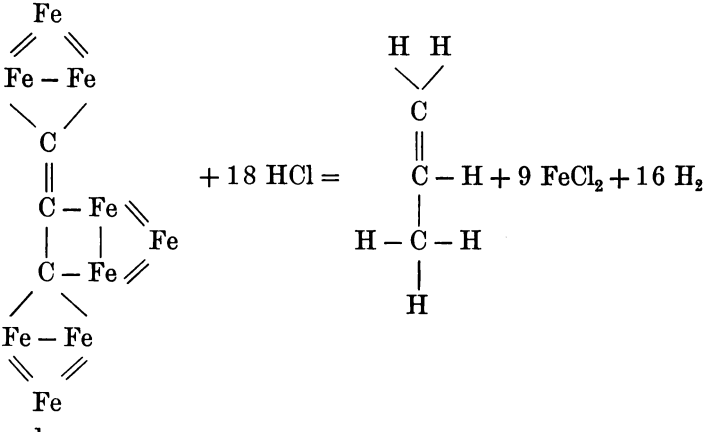
This, however, would furnish methylene, which, up to the present, has not been isolated, and which—containing an unsaturated carbon atom—would either immediately unite with hydrogen to form methane (CH_4), or probably form ethane (C_2H_6) after previously undergoing polymerisation.

The next member of the ferrocarbon series (C_2Fe_6) would furnish the first known member of the olefine series (namely, ethylene, C_2H_4) as the primary product of solution, according to the equation—

[1] Or, more correctly, $Fe\begin{cases}Fe—\\|\\Fe—\end{cases}$



The decomposition of the third member goes on in accordance with the equation—



and so on.

As a matter of fact, however, the decomposition products are not so simple as these equations would imply, being influenced by two known facts, namely—

1. The olefines endeavour to unite with nascent hydrogen to form the corresponding paraffins, according to the equation $C_nH_{2n} + H_2 = C_nH_{2n+2}$. This explains the appearance of large quantities of methane (CH_4), probably together with ethane (C_2H_6), whereas methylene has not yet been isolated at all.

2. The higher olefines exhibit a decided tendency to polymerise under the influence of acids. This tendency is already decidedly visible in the case of propylene, and is particularly pronounced with butylene and the higher members.

The carbon left unrecognised in the earlier researches forms liquid hydrocarbons of high boiling point, which are not removed by steam or hydrogen when the steel is dissolved. Whether these high-boiling hydrocarbons represent primary solution-products, or have been formed by polymerisation and absorption of hydrogen from lower members of the olefine series, has not yet been determined.

With reference to the application of his hypothesis to the theory of steel, Campbell says: "During the last three years I have endeavoured to ascertain what value it (the coefficient n) possesses in the different sorts of steel, and my studies have led, with a fair degree of concordance, to the result that C_4Fe_{12} preponderates in steels with less than 1·3 per cent. of carbon; nevertheless the derivatives obtained have proved, in a fairly certain manner, the presence of C_2Fe_6, C_3Fe_9, and C_5Fe_{15}. The proportion of C_2Fe_6 in annealed steel increases with the carbon content. Moreover, in the steels in question, more C_2Fe_6 appears after hardening than after annealing. Bearing in mind that the solution-products of hardened steel are qualitatively the same as those furnished by the same steel after annealing, it appears fairly certain that the former contains the ferrocarbons (or, as is usually said, iron carbide) in a dissolved state."

The assumption of polymeric iron carbides harmonises per-

fectly with the facts already mentioned, which already indicated the existence of more than two different forms of combined carbon. Particularly interesting, however, is a comparison of the different colouring power of the forms of carbon differentiated by the present author, with the various members of Campbell's polymeric series. According to the latter worker, the carbide C_2Fe_6 predominates in hardened steel; according to the author, the bi-carbon. In annealed steel, Campbell ascribes the predominance to the carbide C_4Fe_{12}; the author giving this position to the tetra-carbon.

Again, Campbell's observation that steel with over 1·3 per cent. of hydrocarbon contained increasing amounts of C_2Fe_6 is confirmed by a comparison of the samples C and G.

Whether the deposited free cementite is identical with that contained in pearlite, can only be ascertained by further examination; nevertheless, a comparison of the samples C and G makes the probability of this very slight.

If we bear in mind the remarkable relation existing between the colour intensity of the three forms of carbon already referred to, and the degree of polymerisation of Campbell's carbides, the endeavour to identify the two series will not appear too venturesome. We should then have—

Behaviour towards cold dilute Nitric Acid.	Colour intensity of the Solution.	Variety of Carbon.	Possibly corresponding Carbide.
Soluble in the cold	2	Bi- carbon	C_2Fe_6
	3	Tri- ,,	C_3Fe_9
Soluble at 80° C.	4	Tetra- ,,	C_4Fe_{12}
—	?	?	C_5Fe_{15}

At anyrate, the carbide C_5Fe_{15} should give a solution with the colour depth 5 (*i.e.* 1·25 the strength of C_4Fe_{12}); nevertheless, according to Campbell, this compound appears only in small quantities, and therefore cannot appreciably alter the colour of the nitric solution of carbide carbon.

CHAPTER VI

APPLYING THE CURVES OF SOLUTION DEDUCED FROM THE CURVES OF RECALESCENCE TO THE DETERMINATION OF THE CHEMICAL COMPOSITION OF THE CARBON PRESENT IN IRON ALLOYS

On referring to the curves of solution of pure iron-carbon alloys, as communicated by Roberts-Austen,[1] and illustrated in Fig. 82, Plate X., we find that the line A B corresponds to the solidification of metallic iron, B D to the deposition of graphite from the liquid metal, and a B c to the solidification of the eutectic alloy. Furthermore—

G O	corresponds to the	critical points	A_1 (deposition of pure iron).
M O	„	„	A_2 (renewed deposition of pure iron).
O S	„	„	$A_{1,2}$ (renewed deposition of pure iron).
S E	...	...	... (depositions of free iron carbide).
P S P′	„	„	A_3 (or $A_{1,2,3}$), *i.e.* the conversion of martensite into pearlite.

Directing attention, in the first place, to the curves illustrating the solidification of the liquid iron-carbon alloys, the first requirement for deducing therefrom the constitution of the carbon is a knowledge of the fusing point of pure iron and its latent heat of fusion. The former of these has not

[1] *Fifth Report to the Alloys Research Committee of the Inst. of Mech. Eng.*, 1899.

been determined with precision, the reports on this question being—

$$T_0 - 273° \text{ C.} = 1587° \text{ C. (Danielle).}$$
$$= 1500° \text{ to } 1600° \text{ C. (Pouillet).}$$
$$= 1804° \text{ C. (Carnellay).}$$
$$= 1600° \text{ C. (Pictet).}$$
$$= 1500° \text{ C. (Osmond).}$$

At the present time it is usually taken as 1600° C.

Still less reliable are the available data with respect to the latent heat of fusion—

Grey pig iron . .	$w = 23$	calories (Gruner, Troilus).
White „ . .	$= 33$	„ („ „).
Steel (estimated) .	$= 20$	„ (Campbell).

True, Person has given the general formula—

$$w = 0{\cdot}00167\ k\ (1 + \frac{2}{\sqrt{d}})$$

for the latent heat of fusion of solid bodies, k representing the module of elasticity, and d the sp. gr.; but, though this formula gives satisfactory values for lead, tin, bismuth, zinc, and silver, it is by no means certain, and the value, $w = 57$ cal., which it gives for iron ($k = 20{,}000$, $d = 7{\cdot}8$), is so high and differs so widely from Gruner's figures, as well as from the latent heat of fusion of nickel ($w = 4{\cdot}64$), the metal so nearly resembling iron, that it appears advisable to assume $w = 20$ cal.[1]

Hence the molecular depression of the solidification point of iron is—

$$E = 0{\cdot}0198 \cdot \frac{T_0^2}{w} = 0{\cdot}0198 \cdot \frac{1873^2}{20} = 3273$$

and, assuming that pure iron is deposited on the solidification

[1] For nickel, $k = 21{,}400$ (*Verh. d. Ver. z. Bef. d. Gewerbefleisses*, 1898); $d = 8{\cdot}60$ (*Pogg. Ann.*, lxxviii. p. 97; Liebig's *Jahresber.*, 1885, p. 294; 1886, p. 283), from which, according to Person's formula, we should have $w = 29{\cdot}91$ cal., or 6·44 times the value actually found. This affords an indirect confirmation of the assumption that $w = 57$ must be too high for iron.

he alloys, according to van't Hoff's equation $M = \frac{E}{t} m$, obtain the following values for the molecular dimensions he carbon dissolved in molten iron at the solidification t:[1]—

Percentage Composition.		Fusing Point, °C.	Depression of Fusing Point, °C.	*m*.	Molecular Weight of Dissolved Carbon. M.	Number of Atoms in Dissolved C-Molecule. *n*.
.	*Fe*.					
	100·0	1600	...	...	...	...
·0	100·0–99·0	1600–1460	0–140	∞–1·01	23·612	1·97
5	98·5	1400	200	1·52	24·875	2.07
8	98·2	1370	230	1·83	22·857	1·90
4	97·6	1300	300	2·46	26·839	2·24
8	97·2	1255	345	2·88	27·323	2·28
4	96·6	1200	400	3·52	28·801	2·40
3	95·7	1130	470	4·49	31·264	2·61

According to these figures, then, iron between 1600° and t 1400° C. would contain in solution diatomic molecules arbon, with which a progressive association of triatomic cules occurs as the temperature falls. At about 1160° he number of di- and triatomic molecules of carbon ent in the solution would be nearly identical. This es thoroughly with the fact that, in general, the composi- of the bodies appearing in solution is the more complex, he molecular weight is the greater the deeper the fall in temperature of deposition. In fact it explains this de- sion in the temperature of deposition, since, as a general the increasing molecular weight of the dissolved body is mpanied (provided this increase in molecular dimensions e result of pure polymerisation, and not of incorporation he second constituent of the solution) by a reduction of number of its molecules as compared with those of the nd constituent, and consequently (in the case of substances

[1] H. v. Jüptner, *Journ. Iron and Steel Inst.*, 1898, 1899; *Stahl und Eisen*, Nos. 11, 12, and 13.

not of unlimited miscibility) a decrease in the possible maximum limit of its intramolecular volume. Hence the solvent power of the first constituent for the second is diminished, and the latter is therefore compelled to separate out.

To be sure, the laws of solution apply "in their strict sense only for dilute solutions, and can only serve for approximate orientation in the case of concentrated solutions (*e.g.* 10 – 20 per cent.)."[1] Nevertheless, in the present instance such dilute (4·3 per cent. of C at the most) solutions are in question, so that even in this respect the result of our calculation may be regarded as probably correct.

On the other hand, however, Heycock and Neville[2] have drawn up a formula also applicable to concentrated solutions, by means of which A. Stansfield[3] finds that the molecules of the dissolved carbon, both in liquid steel and in pig iron, consist of two atoms.

The equation—

$$M = \frac{0{\cdot}0198 \,.\, T}{w}\, m\, \frac{T-\tau}{t} = \frac{0{\cdot}0198+1873}{20}\, m \left(\frac{1873}{t}-1\right)$$

$$= 1{\cdot}85\; m \left(\frac{1873}{t}-1\right)$$

to wit, furnishes the following values:—

m.	$1{\cdot}85m$.	t.	$\frac{1873}{t}$.	M.	n.
1·01	1·8685	140°	13·378	23·127	1·927
1·52	2·8120	200°	9·365	23·522	1·960
1·83	3·3855	230°	8·144	24·186	2·015
2·46	4·5510	300°	6·243	22·761	1·897
2·88	5·3280	345°	5·429	23·598	1·966
3·52	6·5120	400°	4·682	23·977	1·998
4·49	8·3065	470°	3·985	24·795	2·066

[1] Nernst, *Theoretische Chemie*, 1st ed. p. 394. [2] *Journ. Chem. Soc.*
[3] *Journ. Iron and Steel Inst.*, 1899, vol. ii.; see also p. 34 of the present work.

All these calculations, however, apply only when pure iron is deposited on the cooling of the liquid iron-carbon alloy along the line A B. Should this iron, as seems very probable from the microscopical examination, contain dissolved carbon, then the above calculations give results in excess of the truth, *i.e.* the molecule of the dissolved carbon must contain less than two (or 2·6) atoms. Now, as it is impossible for molecules to contain fractions of atoms, it is evident that, under these circumstances, monatomic molecules of carbon must be dissolved in the iron.[1]

It is, however, necessary to examine more closely the phenomena occurring in the cooling of liquid iron-carbon alloys.

In the first place we encounter the problem, Whether the deposition occurring in the course of such cooling consists of pure iron or of a solid solution of iron and carbon?[2] In alloys rich in carbon the latter is undoubtedly the case; but with iron poor in carbon the matter is difficult to decide.

According to Sauveur,[3] the carbon content of martensite varies from 0·12 per cent. (in very mild steel, quenched above the critical temperature) to 0·90 per cent. (in hard steel). Steel with 0·09 per cent. of carbon contains, when quenched above Ar_3, 77 per cent. of martensite and 23 per cent. of ferrite. Therefore above Ar_3, 0·12 per cent. of carbon may unite with 99·80 per cent. of iron, or, in round numbers, 1 part of C with 800 parts of Fe. The martensite cannot take up any more ferrite, and, if the steel contain less than 0·12 per cent. of carbon, the excess of unabsorbed iron is present as free ferrite.

[1] A. Stansfield, *loc. cit.*; nevertheless it is by no means impossible that polyatomic carbon molecules can exist, in addition to the monatomic molecules, in the solution.

[2] H. v. Jüptner, *Journ. Iron and Steel Inst.*, 1899, vol. ii.

[3] *The Microstructure of Steel.*

From this results, according to Sauveur—

Temperature.	Saturation Point (in Martensite) of the—	
	Fe for C.*	C for Fe.
Above Ar_3	?	0·12 per cent. C (1 : 800)
Between Ar_3 and Ar_2	?	0·25 ,, ,, (1 : 400)
Between Ar_2 and Ar_1	?	0·50 ,, ,, (1 : 200)
At Ar_1	0·90 per cent. C (1 : 110)	0·90 ,, ,, (1 : 110)

* The point of saturation of Fe for C in martensite and austenite together is deducible from Fig. 82 as follows:—

690° C. . . 0·82 per cent. C	900° C. . . 1·10 per cent. C
800° ,, . . 0·90 ,, ,,	1000° ,, . . 1·07 ,, ,,
860° ,, . . 1·00 ,, ,,	

With less than 0·12 per cent. of carbon, a little ferrite remains unabsorbed on further heating (above Ar_3).

These reports find confirmation by Osmond's observations,[1] according to which a steel with 0·14 per cent. C, 0·045 per cent. Si, 0·018 per cent. S, 0·01 per cent. P, and 0·19 per cent. Mn, gave—

	Martensite.	Ferrite.	Approximate percentage of Martensite Carbon.[2]	C. : Fe.
Heated to 960° C., quenched at 670° (between Ar_1 and Ar_2)	14	86	1·0	1 : 99·00
Heated to 960° C., quenched at 770° (between Ar_2 and Ar_3)	24	76	0·58	1 : 171·41
Heated to 960° C., quenched at 820° (middle of Ar_3)	46	54	0·30	1 : 332·33
Heated and quenched at 1000° C.	61	39	0·23	1 : 433·78
Heated and quenched at 1340° C.	90	10	0·16	1 : 624·00

[1] Discussion on Sauveur's paper.

[2] The figures show that the solubility of iron in the carbon (or, more correctly, the carbide) of martensite increases considerably as the temperature rises.

It must therefore be left to further investigations at very igh temperatures to determine—

1. Whether we have here to do with an actual limit of turation between iron carbide and iron, or whether the bserved amounts of ferrite cannot probably be explained by ie slowness with which the phenomena of solution and eposition proceed in solid iron ; and

2. Whether, in the case of lower percentages of carbon, rrite still appears also in the immediate vicinity of the sing point.

It seems probable, from the outset, to suppose that the rrite line will traverse the fusing point of the pure iron ;[1] evertheless, an entirely different behaviour could be deduced om the foregoing figures. If, namely, we take the differ- nces in the ferrite content, we have—

Temperature Difference.	Ferrite Difference, per cent.	Diminution of Ferrite per 1° C., per cent.
770 − 670 = 100°	86 − 76 = 10	0·10
820 − 770 = 50°	76 − 54 = 22	0·44
1000 − 820 = 180°	54 − 39 = 15	0·08
1340 − 1000 = 340°	39 − 10 = 29	0·08

The decrease in the amount of ferrite thus attains a aximum at Ar_3, and diminishes rapidly at both higher and wer temperatures, so that there is always a *possibility* of rrite (*i.e.* pure iron) being deposited first, when the iron is ry poor in carbon.

Another point worthy our attention is the query, How uch carbon is contained in the portion of metal solidifying st during the cooling of liquid iron rich in carbon ?

Let us assume that the liquid eutectic alloy contains 4·3 r cent. of C and 95·7 per cent. of Fe, or 22·25 parts of

[1] See Figs. in the author's paper on the solution theory, *Journ. Iron and Steel st.*, 1898, vol. ii.

iron to each 1 part of carbon. If, in alloys poorer in carbon than is the eutectic, the excess of iron were deposited as ferrite, we should have—

Total Carbon.	Eutectic Alloy.	Ferrite.
4·3 per cent.	100·00	0
4·0 „	89·00	11·00
3·0 „	66·75	33·25
2·0 „	44·50	55·50
1·2 „	26·70	73·30

From our experience with steel, this is decidedly incorrect, since we must on the contrary assume that, in the case of alloys rich in carbon, the first to solidify will be, not pure iron, but an iron-carbon solution, whilst the eutectic alloy will not solidify till the last. This iron-carbon solution, however, is probably austenite, the quantitative composition of which is unfortunately unknown. Since, in the course of further cooling, it is converted into martensite, it must contain at least as much carbon as this latter (1 part C to 110 parts Fe at 690° C., and 1 part C to 57·8 parts Fe at 1000° C.).[1] Probably, however, at least in alloys rich in carbon, it contains more carbon, since otherwise the separation of cementite from such kinds of steel would be inexplicable. Still, no approximate calculation can be based on these reports, nothing being known as to the carbon content of saturated martensite at higher temperatures.

By marking down in the graphical sketch, Fig. 82, the three austenite points determined by Osmond, viz.—

Percentage of C.	0 per cent. Austenite.	50 per cent. Austenite.
1·0	above 1000° C.	...
1·5–1·6	„ 740° C.	1140° C.

it becomes evident in the first place that a straight line drawn through the two 0 per cent. austenite points encounters

[1] Deduced from Fig. 82.

the fusing point of pure iron. Even if only accidental, this shows that the temperatures at which iron carbide is stable are higher the larger the excess of iron present (a phenomenon that is moreover very probable), and that the formation of iron carbide, or the conversion of austenite into martensite, is accompanied by absorption of heat.

Be the rest as it may, in any event it is very remarkable that the end of the solidification curve of the liquid eutectic alloy (in Fig. 82) lies to the right of, and not very far away from, the 0 per cent. austenite line. This, in the first place, again confirms the hypothesis that austenite is a solution of elementary carbon in iron, since it is only from such a solution that deposition of graphite can occur.

Assuming that the 0 per cent. austenite curve is actually a straight line, which at anyrate is fairly accurate within the points (1·0 and 1·5 per cent. C.) determined by Osmond, we then have for the composition of martensite—

Temperature.	Percentage of C.	Parts of Fe to 1 part C.	Percentage of Fe_3C.
1130° C.	0·86	115·28	12·90
1040° C.	1·00	99·00	15·00
1000° C.	1·07	92·46	16·05
930° C.	1·20*	82·33	18·00
690° C.	0·82	120·95	12·30

* Possibly a little too high in consequence of a slight deposition of graphite.

Thus we see that, starting from 690° C., the solubility of the carbon, or the carbide, increases up to a maximum at about 930° C., from which point onwards it recedes once more.

Under the assumption that iron at the fusing point contains only austenite, but no martensite, it would appear from an analysis made by Saniter,[1] according to which, molten iron

[1] *Journ. Iron and Steel Inst.*, 1897, vol. ii.

carbide with only 0·05 per cent. of S and 0·15 per cent. of Mn contained, after slow cooling—

Graphite	3·05 per cent.
Combined Carbon . . .	1·22 „
Total .	4·27 per cent.

and therefore corresponded to the composition of the eutectic alloy, that the composition of austenite at 1130° C. is as follows:—

Combined carbon . . .	1·27 per cent.
Iron	98·73 „
Total .	100·00

(Hence there are 77·74 parts of iron to 1 part of carbon.)

If now we take C to represent the total carbon, and C_a, C_m, C_g the portions of carbon appertaining to austenite, martensite, and graphite respectively, we shall then have—

$$C_a + C_m + C_g = C$$

$$76{\cdot}74\ C_a + 118{\cdot}28\ C_m + C_g = 100$$

and hence $$C_m = 2{\cdot}66 - 2{\cdot}10\ C + 2{\cdot}07\ C_g$$

Now, in the case of steel with 1·2 per cent. of C at 1130° C. (since the same contains 50 per cent. of martensite, provided the 50 per cent. austenite curve has been correctly drawn, *i.e.* passes through the fusing point of pure iron),[1] $C_m = \frac{0{\cdot}86}{2} = 0{\cdot}43$ per cent., and thus—

$$0{\cdot}43 = 2{\cdot}66 - 2{\cdot}07\ C + 2{\cdot}04\ C_g$$

$$= 2{\cdot}66 - 2{\cdot}52 + 2{\cdot}07\ C_g$$

wherefore $$C_g = \frac{0{\cdot}29}{2{\cdot}07} = 0{\cdot}14 \text{ per cent.}$$

As a matter of fact, the eutectic curve extends also a little below 1·1 per cent. C, so that a slight deposition of graphite must apparently occur.

This consideration finally leads to settling the carbon content

[1] This must be the case if the assumption that the 0 per cent. austenite curve traverses this point, and that molten iron contains none but elementary carbon, be correct.

in martensite at 1130° C. as 0·86 per cent. at the most, and of austenite 1·27 per cent., the latter therefore containing in round figures one and a half times as much carbon as martensite.[1]

The first attempt to deduce the molecular weight of the dissolved carbon—or, more properly, carbide—from the curves of solution of the solid iron-carbon alloys, was made by the author[2] in the year 1898. Since that time the question has been further developed by Roberts-Austen,[3] on the basis of V. Rothmund's[4] observations that the modifications of molecular condition of a substance in solid solution exactly resemble the modification of the conditions of aggregation in the case of liquid solutions. In solid, chemically pure iron two such modifications occur—for example, at A_3 and A_2. The latent heat of transformation at these points, corresponding exactly to the latent heat of fusion of liquid solutions, has been deduced by Roberts-Austen from the cooling curves for electrolytically precipitated iron. The increase of temperature at the critical points was measured, and this—after introducing a correction for the probable loss of heat—was multiplied by the specific heat of iron. He found the following values for the latent heat of transformation :—

At Ar_3 . . . . $\omega = 2{\cdot}86$ cal.
„ Ar_2 . . . . $\omega = 1{\cdot}0$ „

(The latter figure may possibly be rather inaccurate.)

From the first of these values the molecular depression of the transformation point is calculated, in just the same manner as the molecular depression of the fusing point, to—

$$E_3 = 0{\cdot}0198 \cdot \frac{T_0^2}{\omega} = 0{\cdot}0198 \cdot \frac{(900+273)^2}{2{\cdot}86} = 9525{\cdot}6.$$

[1] These two solutions must be isosmotic (possess the same osmotic pressure), consequently the number of atoms per molecule of dissolved carbon or carbide in austenite and martensite must be as 2 : 3. If, therefore, austenite at 1130° C. contained an equal number of molecules C and C_2, martensite would contain the carbide Fe_3C in solution.

[2] *Loc. cit.* [3] *Journ. Iron and Steel Inst.*, 1899, vol. ii.

[4] *Zeits. für phys. Chemie*, 1897.

Now the line G O is straight, *i.e.* the molecular dimensions of the dissolved carbide suffer no alteration between the points G and O; it is therefore sufficient to take the point O as the basis of calculation. To this point, however, correspond a carbon content of 0·34 per cent. (or 5·10 per cent. of carbide) and a temperature of 765° C. We thus have $m = 5{\cdot}37$ depression of transformation point = 895 − 765 = 130° C., and therefore the molecular weight of the dissolved carbide—

$$M = \frac{E_3}{t} \cdot m = \frac{9525{\cdot}6}{130} \cdot 5{\cdot}37 = 393{\cdot}48.$$

Since the molecular weight of the carbide Fe_3C is 180, and corresponds to 3 atoms, the carbide molecule calculated above must correspond to the formula 2·18 CFe_3, *i.e.* the same must contain in round numbers $6\frac{1}{2}$ atoms.[1] In other words, steel with not more than 0·34 per cent. of carbon, chiefly contains, at Ar_3, the carbide C_2Fe_6, which coincides very well with the results of the earlier observations.

If, on the other hand, we employ the equation of Heycock and Neville—which is also applicable to more concentrated solutions—we have—

$$T = 900 + 273 = 1173^\circ$$
$$C = 0{\cdot}23 \text{ per cent.}$$
$$CFe_3 = 3{\cdot}45 \text{ per cent.}$$
$$m = 3{\cdot}75$$
$$w = 2{\cdot}86 \text{ cal.}$$
$$t = 100^\circ$$
$$M = \frac{0{\cdot}0198\, mT}{2{\cdot}86} \frac{T - t}{t} = 8{\cdot}121m \frac{1173 - t}{t}$$
$$= 30{\cdot}454\ (11{\cdot}73 - 1) = 326{\cdot}771$$

and

$$n = \frac{4M}{180} = 7{\cdot}26$$

[1] 293·48 : 180 = 2·18.

so that the formula 1·82 CFe_3 would correspond to the carbide.

Commencing with a carbon content of 0·34 per cent., the points Ar_3 and Ar_2 coincide, *i.e.* the two molecular modifications of condition sustained by the chemically purer iron separately at Ar_3 and Ar_2 occur simultaneously. This is usually expressed by indicating the corresponding critical point by $Ar_{3,2}$. The theory with regard to the relation between the depression of this point, $Ar_{3,2}$, and the molecular weight of the dissolved iron carbide, is not so simple as formerly. Roberts-Austen based his calculations on the assumption that the osmotic pressure necessary to produce the observed depression of the transformation temperature is equal to the sum of the pressures which would be required to depress each of the points Ar_2 and Ar_3 to a corresponding extent. In this way he arrives at the result that the molecules of the dissolved carbide at the portion O S of the curve correspond to the formula 2·7 CFe_3, *i.e.* that at this point we are probably in presence of a mixture of about 2 molecules of C_2Fe_6 and 3 molecules of C_3Fe_9 (or perhaps of 2 molecules of C_2Fe_6 with 1 molecule of C_4Fe_{12}), a result which equally agrees with our earlier observations.

Here, also, it is advisable to examine, with the help of Fig. 82, the phenomena arising in the cooling of solid iron-carbon alloys.

Whilst, as we have already seen, the liquid eutectic curve extends from right to left as far as the vicinity of the 0 per cent. austenite curve, the curve of deposition of pure cementite, on the other hand, exhibits the remarkable phenomenon that, so far as it has been actually observed, it terminates at only a short distance from the point at which 50 per cent. of austenite and 50 per cent. of martensite were shown by Osmond. Does it not therefore seem as though a further deposition of carbide would no longer

furnish a point of recalescence because the conversion of austenite into martensite is effected slowly, and that for this reason the deposition of the excess of carbide also can only proceed at a very slow rate? The process would have to be imagined as going on in the following manner:—Austenite at 1130° C. contains about 1·27 per cent. of carbon, whilst martensite contains only 0·86 per cent.; when, therefore, in the course of further cooling, a portion of the austenite is converted into martensite, the solvent power of the martensite, it is true, increases slightly up to 930° C.; however, the carbon now entering the same (naturally in the form of carbide) exceeds this, and therefore a portion of the carbon is bound to be deposited (possibly under polymerisation).

That all the alterations of condition as regards solution, etc., sustained by the iron in cooling are liable to modification, as the result of internal tensions set up in the metal when the cooling is accelerated, is a matter of course.

The most recent researches of H. W. Bakhuis Roozeboom on the solidification and conversion points of mixed crystals[1] throw fresh light on the changes of condition occurring in the cooling of steel, and largely support the author's views on the nature of austenite and the course of the austenite curves. Since (according to a private communication) another research of Roozeboom's on these conditions will shortly appear, the matter will be reverted to in a later section of the present work.

[1] *Zeits. für phys. Chemie*, 1899, pp. 385 and 413.

CHAPTER VII

THE CONSTITUENTS OF IRON: IRON

NEXT to carbon, the most important constituent of the iron alloys is undoubtedly the iron itself.

On allowing chemically pure iron to slowly cool down from a temperature above the fusing point, three points of recalescence occur, namely, at about 1600° C., at 895° C., and 765° C. The first of these corresponds to the solidification point, the other two to the critical points Ar_3 and Ar_2. From this it inevitably follows[1] that the pure iron must undergo changes of condition at 895° and 765° C., which can hardly be otherwise than allotropic. Osmond, who was the first to express this view, and defended it with great ability and zeal against a number of opponents, employs Greek letters to indicate the allotropic forms, as follows:—

α-iron is the modification appearing after slow cooling below Ar_2.

β-iron, the form existing, under similar circumstances, between Ar_2 and Ar_3.

γ-iron, the allotropic modification appearing above Ar_3.

The properties of these three forms are given by Osmond as follows:—

γ-iron, non-magnetic, dissolves both elementary carbon and iron carbide.

β-iron, non-magnetic, dissolves neither carbon nor cementite.

α-iron, magnetic, does not dissolve cementite.

[1] Osmond and Werth, "Théorie cellulaire."

Roberts-Austen [1] describes the phenomena occurring during the cooling of liquid electrolytic iron, or the very pure γ-condition of this metal, in the following terms:—"As the liquid mass cools, it solidifies at a temperature of about 1600° C., though the actual point has not yet been determined. When the iron has solidified it exists in a plastic condition, to which Osmond has given the name γ-iron, and in which it is capable of dissolving variable proportions of carbon (0·8–0·9 per cent. at 700° C., 1·5 per cent. at 1000° C.)."

One of the foundations on which the theory of the allotropic condition of iron is based, is the assumption that the phenomena of hardening are due to the existence of certain conditions of the metal which, while stable at high temperatures, and convertible, when cooled slowly, into other conditions, stable at lower temperatures, are maintained when the cooling is effected (as in hardening) rapidly to below the zone of temperature at which the aforesaid conversion takes place. Specially characteristic differences between the hardened and unhardened metal are exhibited in the mechanical properties, and it was therefore of great interest to ascertain the behaviour, in this particular, of iron very poor in carbon. Originally it was assumed by Howe that the tensile strength of nearly pure iron could be trebled by sudden cooling; but R. A. Hadfield and J. O. Arnold showed that the tensile strength of a sample rod of ¼ sq. in. section was only increased by 25 per cent. (from 21–26 tons per square inch). Howe [2] afterwards experimented with seven samples of iron (containing 0·02 per cent. of carbon and 0·1 per cent. of Cu) of a mean sectional area of 0·034 sq. in., which had been quenched at 900° C. in saturated brine (− 6° C.). The increase of tensile strength exhibited in this case was only 27 per cent. (from 22 to 28 tons per square inch). One sample which gave

[1] *Fifth Report to the Alloys Research Committee of the Inst. of Mech. Eng.*, 1899.
[2] *Eng. Ming. Journ.*, lxii. p. 557; lxiii. p. 111.

higher results was regarded by the experimenter himself as unreliable.

In order to strengthen Howe's conclusions, J. O. Arnold[1] took a sample of Swedish iron of the following composition :—

Carbon	0·07 per cent.
Silicon	0·02 ,,
Manganese	0·02 ,,
Arsenic	0·04 ,,
Phosphorus	0·02 ,,
Sulphur	0·02 ,,
Copper	0·01 ,,
Aluminium	0·02 ,,

which he first heated to 900° C., then cooled slowly to different temperatures, and quenched suddenly. The tensile strain tests gave the following results :—

No. of Sample.	Quenching Temperature, °C.	Maximum Load, Tons per sq. in.	Stretch, percentage of 2-in. marked interval.	Reduction of sectional area (contraction), per cent.
Standard.	15	21·42	44·0	80·0
3	400	21·59	43·0	76·8
6	525	22·46	41·0	78·8
8	600	23·02	34·0	76·2
2	650	25·56	31·5	76·8
5	705	26·24	27·5	73·8
11	780	29·79	29·5	70·8
4	820	29·46	27·5	75·4
9	887	32·63	21·5	75·9
1	928	31·35	30·0	76·2

These figures, together with the recalescence curve determined by the Osmond method, are represented graphically in Fig. 83, Plate X.

From this, Arnold concludes that quenching below red heat has but little effect on the mechanical properties of the metal, but that at incipient red heat, above 500° C., a decided critical point occurs, from whence onwards the curve turns sharply upwards; furthermore, that the critical points Ar_2

[1] *Eng.*, 9th July 1897.

and Ar_3 are, *per se*, without influence on the mechanical properties, inasmuch as between 500° and 900° the increase in the tensile strength is proportionate to the quenching temperature. The deviations of the measured tensile strength from the sharply defined curve, which are regarded by Arnold as experimental errors, amount to—

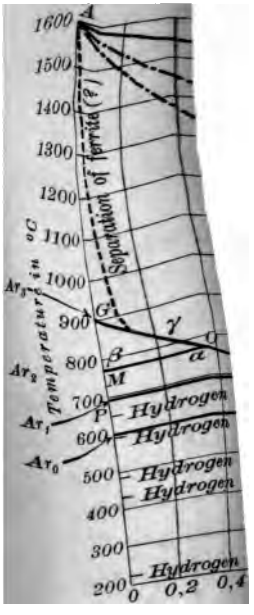
Sample No.	1 =	−0·167 t.
„ „	9 =	+0·067 „
„ „	4 =	−0·033 „
„ „	11 =	+0·100 „
„ „	5 =	−0·050 „
„ „	2 =	+0·050 „
„ „	8 =	−0·060 „
„ „	6 =	+0·060 „

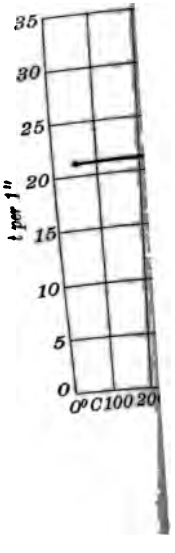
It is worthy of note that the contraction is practically constant (mean, 76 per cent.) for all quenched samples, whereas for normal metal it amounts to 80 per cent.

These conclusions were rightly attacked by Howe, Osmond, and Sauveur. The latter[1] plotted Arnold's tensile test results graphically (Fig. 84, Plate X.), and, as a result of further experience, marked the position of the critical zone Ar_1 between 630° and 645°. He concluded that no noteworthy increase of tensile strength occurs up to 400° C. From 400° to 600° a very gradual and slight increase occurs, which coincides with Howe's observation[2] that the conversion of hardening carbon into cementite carbon continues below Ar_1. At 600°, slightly below Ar_1, the tensile strength is 23·02 tons; at 650°—just above Ar_1—it increases to 25·56 tons, *i.e.* 2½ tons for 50°. When the quenching is effected between Ar_1 and the next critical point, the increase in tensile strength for an accession of 55° is only 0·68 ton. The next test quenched above Ar_2 gave a sudden increase in tensile strength equal to 3½ tons. Between Ar_2 and Ar_3

[1] *Eng. Ming. Journ.*, lxiv. p. 489.
[2] *Journ. Iron and Steel Inst.*, 1895, ii. p. 258.

Jüptner, Prinz





there is no increase (on the contrary, a slight decrease), whereas at Ar_3 the increase is over 3 tons. Further heating results in a decrease of tensile strength. If the samples had approximated more closely, the curve of tensile strength would presumably have assumed the form indicated by the dotted line. Consequently, according to Sauveur, the increases in tensile strength actually coincide with the critical points.

The question of the allotropic forms of iron has been dealt with in a very thorough and lucid manner by H. Le Chatelier.[1] He first shows that the more slowly the iron is heated the lower the temperature at which conversion occurs, and that the converse change ensues at temperatures which are the higher in proportion as the cooling is retarded; so that, given infinitely slow heating or cooling, the two transformation points might coincide.

These facts are in complete harmony with those accompanying all changes in the condition of bodies, especially allotropic conversions, and which we will now proceed to trace in the case of sulphur. This element occurs in two allotropic modifications, differing in their properties, crystalline habit, density, specific heat, heat of combustion, etc. According to their crystalline habit they are known as octahedral and prismatic sulphur respectively. The former is stable in the cold up to temperatures below 95°·6, the other form being stable at higher temperatures. On heating octahedral sulphur above 95°·6 per cent. it is converted, with absorption of heat, into the prismatic form. The conversion, however, does not proceed all at once, but increases in degree the higher the temperature rises, so that the conversion temperature is the higher in proportion as the heat is more rapidly applied. Conversely, the prismatic variety is changed into the octahedral form on being cooled below 95°·6 C. The rapidity of

[1] *Rev. Gén. des Sciences*, 15th Jan. 1897; *The Metallographist*, i. p. 52.

conversion increases at first as the temperature falls, and attains a maximum at about 60°, but sinks rapidly on further cooling, so that at the ordinary atmospheric temperature it is very small, and becomes *nil* at −30° C. On cooling prismatic sulphur quickly to −30°C., it suffers no appreciable alteration, and remains unchanged for any length of time.

In the two varieties of lead oxide—litharge and massicot—the rate of conversion is still more gradual than with sulphur; and massicot, which, under normal conditions, is stable at high temperatures, also remains unchanged at the ordinary temperature. It is, in fact, a general rule, governing all chemical processes, that the rate of conversion is the quicker—

1. The higher its absolute temperature;

2. The greater the interval between the actual temperature and the temperature of equilibrium.

Above the temperature of conversion, both conditions vary in the same direction, and the rapidity increases to an illimitable degree; below the transformation point, on the other hand, they vary in opposite directions, and thus produce a maximum in the rate of conversion.

As we shall see later on, these laws also apply to the hardening process and the conversion of the allotropic modifications of iron.

With regard to the latter, the two most important conversion points were discovered by Osmond, and a third by Hall and Currie. These allotropic conversions are characterised by an absorption of heat during the heating process (Osmond), and by alterations in electrical conductivity (H. Le Chatelier), in magnetic properties (Currie), and in volume. They occur at 740°, 850°, and 1280° C. The first conversion coincides with an almost complete disappearance of the magnetic properties of the iron, and is accompanied by a slight absorption of heat. The position of the conversion point is only slightly in-

fluenced by the method of cooling or heating, so that in both cases it occurs at about the same temperature.[1] The second conversion is characterised by the sudden change in the law according to which the electrical resistance of bodies varies with the temperature.[2] This conversion is influenced to a considerable extent by the mode of heating or cooling employed.

The conversions in question do not occur at the temperatures specified, except when the microscope reveals the presence of free ferrite; consequently they must be in some way connected with this constituent.

On the other hand, however, the labours of H. Le Chatelier on electrical resistance have shown the existence of a modification of condition in the case of steel so rich in carbon as to contain only martensite, and no ferrite; only in this case the conversion temperature lies at or near 800° C., instead of 850°. Unless these observations are erroneous, we must assume that an allotropic conversion also occurs in iron containing martensite, though at a lower temperature than with pure iron. This entirely harmonises with all similar known facts. Thus, for example, that change of condition in water which is evidenced by the occurrence of maximum density, also occurs in aqueous solutions, but at a different temperature. That this change of condition in martensite should have escaped Osmond's notice in the recalescence observations may be due to the slowness with which it is brought about.

With regard to the importance of the conversion point at 1280° C. (Hall and Currie), Le Chatelier is silent.

Perhaps it corresponds to the deposition of ferrite from martensite, which (see Chapter VI.) seems to occur even above Ar_3 in the case of iron poor in carbon.

[1] It corresponds to the point Ar_2.

[2] This increases about tenfold between ordinary temperature and Ar_3, bu remains almost constant above the latter temperature.

According to Howe,[1] an allotropic modification—which he terms δ-iron—also results from cold working the metal. However, the observations made on this point are not yet sufficiently numerous to enable the question to be definitely settled.

Howe bases the assumption of this δ-iron on the influence of cold working, *i.e.* on distorsion, and also on the circumstance that, even in very mild grades of steel with a very low carbon content, a certain hardening is produced on quenching the metal.

He also mentions that cold-worked metal does not exhibit any flow on breaking, and that flow ceases to appear at a temperature of about 500° C. Nevertheless, the effects of distorsion—particularly a raising of the limits of elasticity and expansion—are still apparent up to 632° C. in some cases.

With regard to this latter point it may be mentioned that, at the temperature in question, carbide carbon is already converted into hardening carbon, and that consequently the phenomenon in question could also be attributed thereto.

Reference has already been made in Book II. to the micrographical differences which Saniter believed to have found between the various forms of iron.

[1] *The Hardening of Steel.*

CHAPTER VIII

THE CONSTITUENTS OF IRON ALLOYS: MANGANESE

WHETHER manganese gives solutions isomorphous with iron has not been definitely ascertained, but at anyrate one would not be far wrong in provisionally assuming this to be the case, and, for instance, calculating the fusing point of pure iron-manganese alloys, according to the law of mixtures, from the fusing point of iron (1600° C.) and that of manganese (1900° C.).

For us, the behaviour of manganese towards carbon is of special interest. The first remarkable thing is the great solvent power of this metal in comparison with iron. Whereas the saturation limit of iron for carbon at the fusing point is about 4·6, or according to Saniter 4·8, over 7 per cent. of carbon may be contained in 80 per cent. ferromanganese, as the following analysis shows:—

Carbon	7·079 per cent.
Silicon	0·142 ,,
Manganese	81·154 ,,
Phosphorus	0·412 ,,
Sulphur	0·001 ,,
Iron (difference) . . .	11·212 ,,

This high solvent power is also expressed in the circumstance that manganese opposes the deposition of graphite, as well as in the depression it produces on the critical points. Thus, for example, in presence of 12 per cent. of manganese the conversion temperature for martensite into pearlite is below 0° C.

If now we inquire after the forms in which the carbon appears in manganese, the absence of elementary carbon might be concluded from the circumstance that no deposition of graphite occurs in grades of iron that are rich in manganese. On the other hand, however, manganese steel, according to Osmond, exhibits a microstructure revealing, in addition to ferrite or cementite (according to the carbon content), the presence of a substance more closely resembling austenite than martensite in its properties.

In the chemistry of the subject, mention must first be made of the researches of J. S. Benneville.[1] This worker found that ferromanganese is slightly decomposed by cold water, and readily so, with evolution of hydrocarbons, by boiling water. On solution in hot mineral acids there remains a black residue entirely free from manganese. Cold hydrochloric acid (sp. gr. 1·17) furnishes a considerable amount of a metallic residue, which, after extraction with carbon disulphide and ether, exhibits, under a power of 50 diameters, more or less decided crystalline groups and granular masses with a brilliant metallic lustre. A similar metallic residue is also left on treating the ferromanganese with strong bromine water. Such crystals are also found in the residue obtained by boiling the alloy in ammonium citrate.

De Benneville employed for his researches two kinds of ferromanganese, which he marked A and B. These had the following composition:—

	A, per cent.	B, per cent.
Carbon	...	6·18
Silicon	0·54	0·47
Phosphorus	0·28	0·23
Manganese	78·66	76·44
Iron	15·05	16·84

[1] *Journ. Iron and Steel Inst.*, 1896, vol. i. p. 222.

On treating with hydrochloric acid (sp. gr. 1·17) in large excess, there remained crystals which, after washing with alcohol, carbon disulphide, and ether, re-washing with alcohol, and drying at 125° C., had the following composition:—

	A, per cent.	B, per cent.
Iron	8·40	9·16
Manganese	51·00	61·38
Silicon	2·94	1·10
Carbon	37·56	27·80
Phosphorus	0·10	0·56

On calculating the atomic ratio and picturing the iron combined as Fe_3C, the phosphorus as P_2Mn_3, we then have—

Sple. A	0·15 atom Fe	0·15 Fe	...	...
	0·93 ,, Mn	...	0·045 Mn	0·885 Mn
	0·105 ,, Si	...	...	0·105 Si
	3·13 ,, C	0·05 C	...	3·08 C
	0·003 ,, P	...	0·003 P	...
Sple. B	0·16 atom Fe	0·16 Fe	...	...
	1·11 ,, Mn	...	0·06 Mn	1·05 Mn
	0·04 ,, Si	...	...	0·04 Si
	2·32 ,, C	0·05 C	...	2·27 C
	0·02 ,, P	...	0·02 P	...

As can be seen, the carbon and manganese present in the crystals are not in any atomic ratio, and also not in any approximately similar proportion to that in iron carbide.

By similarly treating a series of samples (20 grms. each) of ferromanganese B with 100 c.c. of hydrochloric acid (sp. gr. 1·19) and variable quantities of water in the cold, he obtained the subjoined results:—

	1	2	3	4	5	6
Total volume of liquid acid solvent in c.c.	100	150	200	300	400	500
Acid, per cent. . .	38·73	29·05	19·37	12·58	9·68	7·75
Weight of residue from 20 grms.	0·87	0·84	2·75[1]	3·33	3·41[1]	2·26
Residue, per cent. . .	4·35	4·20	13·75	10·60	17·00	11·30
Iron, ,, . .	7·85	6·77	11·28	13·49	11·68	17·61
Manganese, ,, . .	41·56	25·78	49·10	57·49	59·62	62·29
Silica,[2] ,, . .	18·15	20·47	4·96	3·42	1·16	3·66
Phosphorus, ,, . .	1·93	2·84	1·09	1·24	0·71	1·31
Carbon, ,, . .	30·40	24·24	17·72	17·82	11·54	4·78

On calculating the atomic ratios of iron, manganese, phosphorus, and carbon, we have—

	1	2	3	4	5	6
Iron	0·14	0·12	0·20	0·24	0·21	0·31
Manganese . . .	0·76	0·47	0·89	1·04	1·08	1·13
Phosphorus . . .	0·06	0·09	0·03	0·04	0·02	0·04
Carbon	2·53	2·02	1·48	1·50	0·96	0·40

and after deducting Fe_3C and Mn_3P_2—

	1	2	3	4	5	6
Mn	0·72	0·41	0·87	1·03	1·07	1·10
C	2·48	1·98	1·41	1·42	0·89	0·30

In the first five cases we therefore have far less, and only in the sixth a little more, manganese than would correspond with the formula Mn_3C.

[1] 1. Amorphous, cellular, granular masses of silica. Colour white, with faint grey tinge. 2. Amorphous cellular granules. White silica resembling pumice, with mixed bronze-coloured metallic granules. 3. Amorphous cellular masses. Metallic, with steel-blue or bronze lustre. No siliceous skeleton present. 4. Amorphous cellular masses. Bronze-coloured and white metallic lustre. Silica, but only in small quantities. 5. Granular metallic masses with steel-blue or bronze-coloured lustre. No silica present. 6. Like 5; silica present.

[2] Partly or entirely present as silicon, as in 4, 5, and 6.

The researches show that the residue after solution is not a homogeneous body, the granular portion being a complex substance. It is also evident that a considerable portion of the silicon present in the alloys is in the form of silicide. Nearly the whole of the manganese was dissolved. A portion of the carbon was liberated in the form of hydrocarbons.

Very different results were furnished by treating ferromanganese with strong aqueous solutions of bromine and iodine. Silicon and phosphorus are present in small quantities. Unfortunately, no estimation could be made of the carbon in the residue.

Since the amount of iron is insufficient to combine with the whole of the phosphorus to form PFe_3, it is probable that manganese phosphide is also present.

The examination of the residue gave—

Seven days' cold digestion with excess of strong aqueous solutions of Br or I.	Bromine.				Iodine.			
	Ferromanganese.				Ferromanganese.			
	A		B		A		B	
	Percentage in—							
	Residue.	Ferromanganese.	Residue.	Ferromanganese.	Residue.	Ferromanganese.	Residue.	Ferromanganese.
Iron . . .	0·48	3·19	0·59	3·50	0·49	3·19	0·50	2·90
Manganese . .	0·44	0·64	0·59	0·77	...	...	...	...
Silicon . . .	0·40	74·1	0·19	40·4	0·17	31·5	0·17	36·2
Phosphorus . .	0·12	48·0	0·12	48·0	0·08	32·0	0·08	34·8

Whereas, according to the analysis, the residues from the treatment of ferromanganese with hydrochloric acid could not contain any carbon compounds with hydrogen or hydrogen and oxygen, the presence of such is quite possible in the

residues from the above bromine or iodine treatment, the more so because we have found similar decomposition products in the case of iron carbide.

De Benneville's researches also extended to the gases evolved in dissolving ferromanganese. Dilute sulphuric acid (sp. gr. 1·17) was selected as the solvent on account of its non-volatility; solution was effected in the cold. No notice was taken of the relation between the weight of metal dissolved and the volume of gas liberated. As these experiments gave no weighty results, it is sufficient to merely mention them here.

T. W. Hogg[1] treated ferromanganese with a large excess of dilute nitric acid (sp. gr. 1·2) in the cold, and obtained a residue which, after filtering and drying over concentrated sulphuric acid, had the following composition:—

Carbon	40·36 per cent.
Water	35·73 „
Nitrogen	9·50 „
Mineral matters . . .	7·80 „
Oxygen (difference) . .	6·61 „

The water furnished by combustion was not calculated to hydrogen. This analysis furnishes, on calculation, the atomic ratio—

Carbon	3·365 or 6·02
Hydrogen	3·970 „ 7·13
Oxygen	2·398 „ 4·30
Nitrogen	0·557 „ 1·00

It was found that this substance undergoes decomposition even at the ordinary temperature. To obtain further information on this point, a current of dry air was passed over the substance at different temperatures for half an hour each time, which treatment gave—

[1] *Journ. Iron and Steel Inst.*, 1896, vol. ii. p. 179.

	Temperature C.			
	80° per cent.	100° per cent.	130° per cent.	160° per cent.
Loss in weight.	3·1	16·35	22·75	38·75
Absorbed by $CaCl_2$	2·1	10·65	14·55	19·7
,, KHO	1·2	6·25	8·90	18·7
Total	3·3	16·9	23·45	38·4
Excess of amount absorbed over loss in weight	0·20	0·55	0·70	...

The experiment was abandoned at 160° C. on account of the sudden decomposition of the substance. The substance, dried over sulphuric acid, was next heated to 150° C., whereupon it gave—

Loss in weight	25·37	per cent.
Absorbed by $CaCl_2$	12·85	,,
,, KHO	14·85	,,
	27·70	,,
Excess of amount absorbed over loss in weight	2·33	,,

The caustic potash, after the absorption, contained small quantities of cyanogen, and only a little CO_2, the bulk of the absorbed matter being oxides of nitrogen.

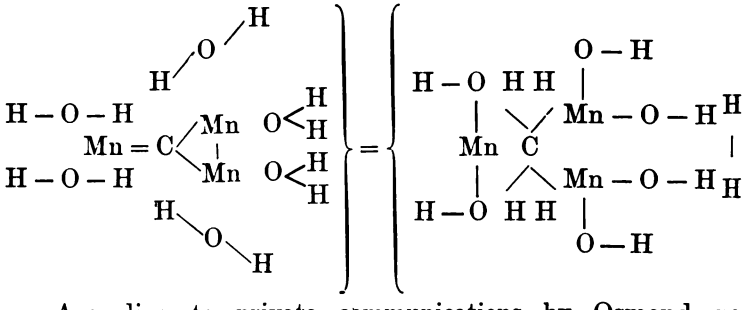
It will be evident that the existing results are insufficient to enable any extensive conclusions to be drawn as to the relations between manganese and carbon in iron alloys. From the foregoing it appears certain that a manganese carbide exists in ferromanganese; but whether elementary carbon is also present, or whether—as in the case of iron—there are several carbides—perhaps polymeric—still remains undetermined. Nevertheless, the assumption that not un-

important amounts of elementary carbon may occur in solution, at least in alloys not too rich in manganese, is favoured by the appearance—as already mentioned—of a structural constituent very similar to austenite in all its properties.[1]

Manganese carbide (Mn_3C) was obtained by Troost and Hautefeuille on fusing manganese in a crucible lined with charcoal. Analysis gave 6·70 per cent. of carbon.[2] H. Moissan[3] obtained it in the electric furnace; it has the sp. gr. 6·89, and decomposes water at the ordinary temperature in accordance with the equation—

$$Mn_3C + 6H_2O = 3Mn(OH)_2 + CH_4 + H_2.$$

It is therefore probable that the molecule contains only a single carbon atom. The decomposition could be explained by the following equation :—



According to private communications by Osmond, no double carbide of iron and manganese exists; the two carbides are said to be able to replace one another in the mixed carbide $(Fe,Mn)_3C$. Only Fe_3C is dissociated at high temperatures, not Mn_3C; the latter therefore imparts stability to the mixed carbides.

[1] Moreover, it is by no means impossible that the solutions of the monocarbides (CFe_3, $CuMn_3$) behave in the same manner as the solutions of elementary carbon in iron or manganese, *i.e.* furnish austenite, whereas only the solutions of the polycarbides (C_nFe_{3n}) yield martensite.

[2] *Compt. rend., séance du* 12th April 1875.

[3] *Ibid.*, vol. cxxii. p. 421, 24th February 1896.

The following reports by Osmond furnish information as to the influence of manganese on the position of the critical points:—

Composition.			$Ar_{2,3}$.			Ar_1.		
C, per cent.	Si, per cent.	Mn, per cent.	Limit.	Maximum.	Limit.	Limit.	Maximum.	Limit.
0·29	0·06	0·27	780°	720–715°	690°	680°	660°	640°
0·32	0·05	0·50	740°	705–697°	660°	660°	640°	620°
0·42	0·035	1·00	725°	665°?	Coincident.		625°	600°
0·46	0·07	1·08	725°?	658°?	,,		620°	595°
...	...	20·00	No critical point noticeable.					
...	...	50·00	,,			,,		
...	...	80·00	,,			,,		

CHAPTER IX

REMAINING CONSTITUENTS OF IRON ALLOYS

A. Silicon

Whereas it was formerly believed that iron could contain graphitic silicon, Turner [1] subsequently proved that this is not the case.

The presence of iron silicide in commercial iron has been demonstrated by Morton.[2]

According to Drown,[3] the progress of the reaction occurring between acids and silicon when iron alloys are dissolved therein, depends on the concentration of the acids. Strong acids deposit much insoluble silica, whilst dilute acids retain a considerable quantity in solution. Silicon is also often found, otherwise than as silica, in solution residues. A distinction must therefore be drawn between such as is unattacked and such as is oxidised during the dissolving of the metal.

In dissolving ferrosilicon (poor in manganese) in dilute sulphuric acid, Carnot and Goutal [4] obtained a residue consisting chiefly of carbon, various silicides and hydrated silica. The latter they hold to be a decomposition product of certain silicides. Boiling with dilute caustic potash dissolved the

[1] Jordan and Turner, *Journ. Chem. Soc. Trans.*, xlix. p. 215; Turner, *Journ. Iron and Steel Inst.*, 1888, i. p. 28.

[2] *Journ. Iron and Steel Inst.*, 1874, i. p. 102.

[3] De Benneville, *Journ. Iron and Steel Inst.*, 1896, i. p. 238.

[4] *Oesterr. Zeits. f. Berg- u. Hüttenmesen*, 1898, p. 592.

silica and the silicide FeSi; the resulting ferric hydroxide was eliminated by treatment with dilute sulphuric acid, the residue being collected on a filter, washed, dried, lightly calcined, and extracted with a magnet. The magnetic portion had the composition—

Silicon . .	19·75 per cent.	19·86 per cent.
Iron . .	79·63 „	79·84 „
Total .	99·38	99·70

or, in atomic proportions—

Silicon	0·7054	0·7093
Iron	1·4220	1·4257

It therefore agreed with the formula Fe_2Si.

A similar examination of products rich in silicon and manganese gave the following results:—

	Percentage.				
Iron . . .	68·25	68·60	68·80	69·15	71·22
Manganese .	15·10	14·70	16·30	16·80	14·58
Silicon . .	15·40	15·80	14·10	14·04	14·00
	98·75	99·10	99·20	99·99	99·80

or, in atomic proportions—

Iron . . .	1·2188	1·2250	1·2285	1·2348	1·2717
Manganese .	0·2746	0·2673	0·2964	0·3055	0·2651
	1·4934	1·4923	1·5249	1·5403	1·5368
Silicon . .	0·5500	0·5645	0·5035	0·5014	0·5000

which well agrees with the formula $(Fe,Mn)_3Si$.

Finally, under similar treatment, ferromanganese gave a magnetic residue of the composition Fe_2Si.

From this, Carnot and Goutal conclude that iron may contain the silicides FeSi and Fe_2Si; in iron alloys rich in

manganese, however, $(Fe,Mn)_3Si$ may also occur. This latter contains considerable quantities of manganese.

H. Moissan prepared the silicides FeSi and Fe_2Si by artificial means. The latter appears as short prismatic crystals, of sp. gr. 4·851, and is formed even below the fusing point of pure iron. According to G. de Chalmont,[1] it is non-magnetic, and is barely attacked by aqua regia. By heating iron filings with sand and charcoal, this worker obtained crystals of the formula Fe_3Si_2; white, hard, brittle, only faintly magnetic, good conductors of electricity, of sp. gr. 6·36, and but slightly attacked by cold aqua regia ($1HNO_3$: 3HCl), which principally dissolved the iron. They are quickly decomposed by HCl. Colson[2] prepared the compound Fe_6Si_2C (presumably $3Fe_2(Si,C)$, *i.e.* an iron silicide in which Si is partly replaced by C).

The author[3] made an attempt to determine the molecular dimensions of the iron silicide occurring in iron alloys.

B. Phosphorus

As is well known, a given percentage of phosphorus produces different effects in different kinds of iron. Leaving out of consideration pig iron—for which, in view of its method of use, cold shortness is a matter of minor importance—steel and all kinds of ingot iron are very susceptible in this connection. Hard, and especially soft, kinds of refinery iron are less susceptible, and soft puddled iron least of all. Thus, whereas for example, according to P. von Tunner,[4] the analysis of the best hard grades of steel reveals only 0·01 to 0·02 per cent. of phosphorus, and a much inferior grade is characterised by 0·03 to 0·06 per cent., good refinery iron may contain 0·2 to 0·3 per cent., and puddled iron may contain occasionally as much

[1] *Journ. Amer. Chem. Soc.*, xvii. p. 923, 924.
[2] *Compt. rend.*, xciv. p. 1316.
[3] *Journ. Iron and Steel Inst.*, 1899, i. p. 204.
[4] *Oesterr. Zeits. f. Berg- u. Hüttenmesen*, 1887, xix. 227.

as 0·5 per cent. and more phosphorus without being regarded as other than good.

In explanation of this phenomenon, Akerman has pointed out that all cold-short grades of iron—similar to burnt iron—are of coarse crystalline fracture, flaky, and of high lustre, and that their low tensile strength may be attributed to this crystalline structure. Since steel already exhibits a greater tendency to crystallisation, as a result of its higher carbon content, a smaller percentage of phosphorus suffices to render it crystalline. In consequence of the liquid condition they attain during preparation, especially when cooled slowly, all kinds of cast and ingot steel, and even ingot iron, tend to crystallise, and therefore are more susceptible to the influence of phosphorus in this connection. Prolonged heating also produces crystallisation, and therefore cold-shortness, in iron, as is shown in burnt iron, this result ensuing the more readily and completely the higher the temperature employed. Suitable mechanical working of the metal eliminates the flaky, coarsely crystalline texture, and that the more readily and perfectly the lower the proportions of phosphorus and carbon present.

In contrast to this theory, which agrees very well with practical experience, B. W. Cheever[1] would ascribe the divergent action of a given percentage on different kinds of iron and steel to the existence of two forms of this element in the metal: as phosphide and phosphate (the latter in the accompanying slag). Though this is undoubtedly the case, and it must also be admitted that this explanation is very attractive at the first glance, the hypothesis is, nevertheless, entirely inadmissible, as has been shown by L. Schneider,[2] inasmuch as, on the one hand, the analytical methods employed by Cheever are open to objection, and, on the other hand, because the percentage of phosphorus corresponding to the enclosed slag

[1] *Trans. Amer. Inst. Ming. Eng.*, October 1886.
[2] *Oesterr. Zeits. f. Berg- u. Hüttenmesen*, 1887, xxxi. p. 361.

in puddled iron cannot very well exceed 0·002 per cent. of the weight of the steel, and is therefore entirely negligible in comparison with the harmless 0·3 per cent. of phosphorus already present in the material.

The author[1] has made an attempt to solve this problem. It is a well-known fact that iron—at least pig iron rich in phosphorus—when dissolved in dilute acids, furnishes phosphuretted hydrogen, in addition to hydrogen, hydrocarbons, etc., as is readily perceptible from the smell of putrefying marine animals evolved. It has also long been known that on dissolving the most divergent kinds of iron in hydrochloric acid there remains an insoluble residue, which, in addition to graphite, silica, titanic acid, and iron chromide, may also contain iron phosphide and iron carbide.

L. Schneider[2] succeeded in isolating the readily fusible phosphorus compound by means of an aqueous solution of copper chloride, which acts only very slowly on iron phosphide, though rapidly dissolving both pure iron and iron alloys. He examined spiegeleisen (a), white pig iron (b, c), grey pig iron (d, e), white spiegel pig iron (f, g), and ferromanganese (h), of the following composition:—

	Percentage.							
	a.	b.	c.	d.	e.	f.	g.	h.
Chemically combined carbon .	3·3	...	3·56	...	0·55	...	3·98	5·28
Graphite . .	...	...	...	2·2	2·85	...	...	...
Phosphorus . .	2·5	1·45	0·53	1·48	0·94	3·01	3·4	0·13
Silicon . .	0·06	...	0·07	4·0	1·8	0·46	0·89	trace
Manganese . .	0·2	...	2·47	trace	0·07	4·33	18·15	28·7
Sulphur . .	0·44	...	0·028	,,	0·01	trace	...	trace
Copper . .	...	...	0·03	,,	0·01	,,	...	,,
Titanium . .	...	...	...	0·15	...	...	...	...
Iron . . .	...	...	...	...	...	...	...	65·8

[1] *Oesterr. Zeits. f. Berg- u. Hüttenmesen*, 1894, xviii. p. 209; *Journ. Iron and Steel Inst.*, 1897, vol. i. p. 224; *Stahl u. Eisen*, 1897, No. 13.

[2] *Oesterr. Zeits. f. Berg- u. Hüttenmesen*, 1886, p. 736.

The dissolved residue contained—

To—	Percentage.							
	a.	b.	c.	d.	e.	f.	g.	h.
Iron . . .	100	100	100	100	100	100	100	100
Phosphorus . .	18·6	18·6	18·2	18·2	18·5	20·5	37·7	38·8
Manganese . .	...	...	...	...	...	5·7	52·8[1]	54·4

Except when large quantities of manganese are present, all kinds of pig iron therefore furnish iron phosphide, of the composition Fe_3P, when treated with copper chloride. In presence, however, of large quantities of manganese, the percentage of phosphorus rapidly increases with the manganese content, the formula then becoming Mn_3P_2.

In the kinds of pig iron examined, the iron phosphide was found solely in the condition of a pulverulent crystalline admixture, whilst the matrix forming the structure was poor in phosphorus. Consequently phosphorus favours the crystallisation of the more refractory constituents of the iron by the formation of readily fusible compounds, which, being the last to solidify, are not in a position to separate in large crystals. The same phosphorus compounds were also detected by the author in steel and bar iron.

He then started on a new track by more closely examining the gases evolved during the treatment of solution with dilute acids. The gases were passed through two Peligot tubes charged with a neutral solution of silver nitrate of known strength; the flow of gas was regulated by an aspirator. The reactions then occurring are as follows:—

The liberated sulphuretted hydrogen forms silver sulphide, according to the equation—

$$H_2S + 2AgNO_3 = Ag_2S + 2HNO_3,$$

[1] Silicon = 0·7 per cent.

whilst the phosphuretted hydrogen gas decomposes the solution, with formation of phosphoric acid and deposition of metallic silver—

$$8AgNO_3 + PH_3 + 4H_2O = 8Ag + 8HNO_3 + H_3PO_4.$$

Since arseniuretted hydrogen would act in the same way as phosphuretted hydrogen—

$$(12AgNO_3 + 2H_3As + 3H_2O = 12Ag + 12HNO_3 + As_2O_3)$$

the iron sample in question must be first tested for arsenic.

(Antimoniuretted hydrogen also precipitates silver, according to the equation—

$$3AgNO_3 + SbH_3 = Ag_3Sb + 3HNO_3).$$

The silver solution employed must not be ammoniacal, because the acetylene possibly present among the hydrocarbons would then precipitate silver acetylide).[1]

According to the foregoing, the precipitate formed in the silver solution by the gases liberated during the solution of iron by dilute hydrochloric acid or sulphuric acid, consists of silver sulphide and metallic silver.

On filtering the silver solution through glass wool, and titrating the silver in solution with ammonium sulphocyanide, the difference gives the sum of the silver thrown down in the metallic state and in combination with sulphur. On treating the residue on the filter (and any left adhering to the walls of the Peligot tube) with dilute nitric acid, the metallic silver alone is dissolved. This can now also be titrated with ammonium sulphocyanide, whereas the silver sulphide remains behind undissolved, and can therefore be estimated by difference.

As now, according to the foregoing equations, 8 atoms of silver correspond to 1 atom of phosphorus, and 2 atoms of silver to 1 atom of sulphur—

[1] According to recent experiments by H. Behrens, however, no acetylene appears on dissolving iron-carbon alloys in dilute acids.

1 part by weight of Ag = 31 ÷ 8 × 108 = 0·0359 of phosphorus,
1 „ „ = 32 ÷ 2 × 108 = 0·148 of sulphur.

In the phosphorus determinations given below, dilute sulphuric acid of sp. gr. 1·1 (at 18° C.) was selected for dissolving the strips of metal, the operation being started in the cold, then heated to boiling, and finally, after complete solution, a current of air was passed through the apparatus for about nineteen minutes. The silver solution, of which each of the Peligot tubes was charged with 20 c.c., contained 0·00924 grm. per c.c.

Since nitric acid is formed during the decomposition of silver nitrate by either sulphuretted or phosphuretted hydrogen, this acid must in time, although dilute, act as a solvent on the metallic silver, as is shown by the following figures obtained with one and the same material. The titration of the metallic silver was performed at widely different intervals after complete solution occurred; the weights of silver are given in percentages of the substance examined.

terval between Completion of Solution and Titration.	Ag, per cent.	Equivalent Amount of Phosphorus, per cent.
Immediately . . .	0·4749	0·01705
6 hours	0·3683	0·01322
12 „	0·3138	0·01127
72 „	0·2318	0·00832

At anyrate, these figures show that the error resulting from the re-dissolution of the reduced silver is fairly insignificant when the titration is performed immediately after precipitation. The amount of substance taken was between 0·6 and 3 grms.

The following tables contain a few of the values obtained by the method described above:—

A. Pig Iron.

No. of Sample.	C. per cent. Determined Gravimetrically.	P. per cent. Determined Gravimetrically.	Weight taken, grms.	Ag. Precipitated by PH_3 in per cent. of Substance.	Phosphorus, per cent. Liberated as PH_3.	Phosphorus, per cent. Undissolved. Estimated by—Difference.	Phosphorus, per cent. Undissolved. Estimated by—Gravimetry.	Remarks.
1	2·385	0·1315	0·6521	0·7324	0·0623	0·1052	...	White pig iron.
2	3·418	0·0744	1·7117	0·733	0·0026	0·0718	0·0725	Dark grey pig.
3	3·418	0·0744	0·7660	0·1604	0·0058	0·0686	...	Solvent used: H_2SO_4 diluted with equal vol. of H_2O.
4	2·296	1·048	0·3375	1·0679	0·0383	1·0097	...	"Panzerguss" for fire bars.

B. Ingot Iron, Puddled Iron, and Steel.

5	0·2254	0·0970	0·6036	0·1516	0·0054	0·0916	0·0906	Short.
6	0·1800	0·0596	1·0895	0·0550	0·0020	0·0576	...	
7	0·1510	0·0690	1·3583	0·0333	0·0012	0·0638	...	
8	0·239	0·1010	1·5253	0·0005	...	0·1010	0·1120	Good material.
9	0·259	0·0860	1·7266	0·0404	0·0015	0·0845	...	
10	...	0·0964	1·6557	0·4514	0·0162	0·0802	0·0789	Very short.
11	0·273	0·0469	2·4316	0·1504	0·0054	0·0415	...	Slightly cold-short.
12	0·308	0·1242	2·6820	0·6758	0·0243	0·0999	...	Cold-short.
13	0·343	0·5649	2·0424	0·6902	0·0248	0·5401	...	
14	0·122	0·6212	3·0138	0·5002	0·0190	0·6022	...	
15	0·375	0·0847	2·7547	0·4749	0·0171	0·0676	...	Cold-short, the tendency increasing seriatim.
16	0·217	0·0677	2·0870	0·5147	0·0184	0·0493	0·0487	
17	0·168	0·0704	5·6423	0·4932	0·0177	0·0527	0·0539	
18	0·137	0·0648	5·5673	0·6074	0·0218	0·0370	...	
19	0·220	0·0829	1·9924	0·6065	0·0218	0·0611	0·0617	

As these figures show, especially Nos. 15 to 19, the increase in cold-shortness is accompanied by an increase in that portion of the phosphorus which is disengaged as phosphuretted hydrogen when the metal is treated with dilute acids. Thus, for instance, whilst Nos. 8 and 9, with 0·101 per cent. and 0·086 per cent. of total phosphorus (of which but 0 and 0·0015 per cent. are liberated as phosphuretted hydrogen), represent excellent material without any trace of

cold-shortness, the samples Nos. 11, 15, 16, 17, 18, and 19, though having a lower (considerably so in some cases) percentage of total phosphorus (namely, 0·0469, 0·0847, 0·0677, 0·0704, 0·0648, and 0·0829 per cent.), exhibit a decided, and in part very considerable, degree of cold-shortness; these, however, on solution in dilute acids, liberate far more phosphorus in the form of phosphuretted hydrogen (namely, 0·0054, 0·0171, 0·0184, 0·0177, 0·0218, and 0·0218 per cent.) than the first-named samples.

The explanation of this phenomenon is that a portion (fluctuating according to circumstances) of the total phosphorus in iron and steel is separated out in the form of granules of iron phosphide (Fe_3P) or manganese phosphide (Mn_3P_2), whilst the rest of the phosphorus remains more or less evenly distributed throughout the residual matrix. Now, whereas the latter (which is evolved in the form of gaseous phosphuretted hydrogen on treating the metal with dilute acids) naturally influences the mechanical properties of the material in a considerable degree, the insoluble granules of phosphide crystals which are scattered through and surrounded by the matrix, have little or no influence on the mechanical properties of the material, though, by reason of their great hardness, they may, under certain circumstances, become unpleasant in the subsequent working of the metal (turning, etc.).

Now, as according to the foregoing data, the granules of manganese phosphide (Mn_3P_2) contain twice as much phosphorus as the particles of iron phosphide (Fe_3P), the deposition of phosphorus in the form of phosphide granules must be facilitated by the presence of manganese; *i.e.* manganese counteracts the evil effects of phosphorus—which is a fact that has long been known.

Furthermore, it is highly probable that the dimensions of

the phosphide granules are the greater, and therefore the more readily noticeable during the turning or other working of the metal, the more fluid—*i.e.* the hotter—the material has been, and the slower the cooling process; the more time therefore there was for the phosphide granules to form. In the converse case (the amount of deposited phosphide being equal) the granules would be much smaller but more numerous.

The author examined two samples of welded iron, which fully confirmed the opinions expressed above. The examination gave the following results:—

Chemical Composition.	A, per cent.	B, per cent.
Carbon	0·110	0·123
Silicon	0·105	0·103
Manganese	0·097	0·094
Sulphur	0·025	0·022
Phosphorus	0·4423	0·4557
Breaking strain, in tons per sq. in.	28·06, 25·71, 27·11, 28·13, 26·03 } 27·0	19·17, 29·21, 18·79 } 22·4
Expansion per cent. (in a 2-inch interval)	10·0, 8·0, 10·0, 4·0, 10·0 } 8·40	12·0
Sectional contraction, per cent.	37·6, 11·7, 31·4, 28·3, 37·6 } 29·32	25·6
Remarks	Easily welding. Very high cold-shortness.	Easily welding. High cold-shortness.

Since, notwithstanding its lower percentage of total phosphorus, the material A exhibited far greater cold-shortness than B (both being in the natural state of hardness), a determination was made, in both samples, of the amount of phosphorus liberated as phosphuretted hydrogen on treatment

with dilute acids, and of that left behind insoluble. In order to investigate the alteration produced in the condition of the phosphorus by hardening and annealing, the material was heated to about 1000° C. and examined both after sudden quenching in cold water and after slow cooling. The phosphorus contained in the phosphides was estimated by dissolving in nitric acid of sp. gr. 1·2 the residue left on treating the material with dilute sulphuric acid (1 vol. concentrated acid plus 10 vols. water); the product was oxidised with permanganate, the resulting precipitate of manganese peroxide dissolved with a few grains of oxalic acid, then treated with ammonium nitrate and precipitated with molybdenum solution. The results were as follow:—

Condition of Sample.	Percentage of Phosphorus.	A.		B.	
		In per cent. of Sample.	In per cent. of Total P.	In per cent. of Sample.	In per cent. of Total P.
Annealed	Liberated as PH_3	0·3425	77·66	...	...
	Deposited as phosphide	0·0998	22·34	...	...
	Total	0·4423	100·00	...	...
Natural hardness	Liberated as PH_3	0·3553	80·33	0·2887	63·35
	Deposited as phosphide	0·0870	19·67	0·1670	36·65
	Total	0·4423	100·00	0·4557	100·00
Annealed and hardened in cold water	Liberated as PH_3	0·3677	83·13	0·3133	68·75
	Deposited as phosphide	0·0746	16·87	0·1424	31·25
	Total	0·4423	100·00	0·4557	100·00

This table also shows that a larger amount of phosphorus, liberated as phosphuretted hydrogen on dissolving the metal in dilute acids, corresponds with greater cold-shortness;

further, that the amount of deposited phosphides is greater after annealing and smaller after hardening than it is with the same metal in the natural state of hardness. Consequently we are fully justified—the case being analogous to that of the different modifications of carbon—in terming the phosphorus liberated as PH_3 "injurious" or "hardening" phosphorus, and the modification insoluble in dilute acids "phosphide" phosphorus.

The mutual transformation of these two forms of phosphorus occurs in exactly the same way as with the corresponding forms of carbon, only that in the former it apparently does not extend so far as, and proceeds more slowly than, in the latter.

Furthermore, it seems very probable—and has indeed been confirmed by the experiments of H. Behrens and van Linge [1]—that the phosphides are embedded within the carbides.

From the fact that the hardening capacity of steel is diminished by an increasing percentage of phosphorus, it has been rightly deduced that phosphorus favours the deposition of carbide. On the other hand, the injurious influence of phosphorus increases with the percentage of combined carbon, particularly hardening carbon.

One might be inclined to conclude from this the existence of a special chemical relation between these two elements; but, apart from this, it is nevertheless possible that the phenomenon is mostly due to physical causes alone—by increasing the amount of the readily fusible (and longest in solidifying) portion of the alloy, the resulting facilitation of crystallisation, and by the difference between the solidifying points of the phosphides and carbides.

On calculating from the last table the relation between

[1] Fresenius, *Zeits. f. analyt. Chem.*, xxxiii. p. 513.

the phosphide phosphorus, in the natural condition of hardness (P_n) and after hardening in water (P_h)—

$$\text{Sample A. } \frac{P_n}{P_h} = \frac{0{\cdot}0870}{0{\cdot}0746} = 1{\cdot}166$$

$$\text{Sample B. } \frac{P_n}{P_h} = \frac{0{\cdot}1670}{0{\cdot}1424} = 1{\cdot}172,$$

it will be found almost the same in both cases; and the probability is that the separation of the phosphides, with different percentages of phosphorus, proceeds in inverse ratio to the energy of the hardening process.

Mention may here be made of some older researches by Osmond and Werth,[1] wherein the content of phosphorus in a condition such as to be capable of liberation in the form of PH_3 was estimated by absorption with silver nitrate solution. The results are contained in the following table, to which there has been added merely a single column showing the difference (*i.e.* phosphide phosphorus) between the total phosphorus and that liberated as PH_3:—

Material.	Composition.					P, liberated as PH_3.	P, not liberated as PH_3 (=Phosphide P).
	C, per cent.	Mn, per cent.	Si, per cent.	S per cent.	P, per cent.		
ACID BESSEMER STEEL.							
Before adding spiegeleisen	...	...	...	...	0·065	0·044	0·021
After adding spiegeleisen	...	...	...	...	0·065	0·028	0·037
BASIC BESSEMER STEEL.							
Before adding spiegeleisen	...	...	...	0·038	0·046	0·030	0·016
After adding spiegeleisen	...	...	...	0·022	0·046	0·018	0·028

[1] *Théorie cellulaire, Mém. de l'Artillerie de la Marine*, 1887, vol. ii. p. 273.

Material.	Composition.					P, liberated as PH_3.	P, not liberated as PH_3 (= Phosphide P).
	C, per cent.	Mn, per cent.	Si, per cent.	S, per cent.	P, per cent.		
MARTIN STEEL.							
Before adding spiegeleisen	...	...	...	...	0·033	0·022	0·011
After adding spiegeleisen	0·49	0·37	0·075	0·024	0·041	0·014	0·027
Hardened . .	0·49	0·37	0·075	0·024	0·041	0·013	0·028
Very mild steel .	0·18	0·10	...	0·060	0·070	0·049	0·021
Diamond steel No. 1	1·17	0·18	0·44	0·018	0·033	0·005	0·028
Ordinary Bessemer steel	0·50	0·59	0·11	0·042	0·065	0·030	0·035
Ordinary Bessemer steel	0·49	0·74	0·23	0·022	0·065	0·026	0·039
Pig iron . . .	...	...	...	...	0·055	0·041	0·014
Burnt iron from the Moselle, in pseudo-crystals	0·11	trace	0·058	0·032	0·810	0·147	0·663
Spiegeleisen . .	4·00	19·84	...	...	0·145	0·004	0·141
Basic Bessemer pig iron	3·00	2·16	1·71	0·13	2·500	0·037	2·463
Refinery pig iron .	3·00	0·07	0·37	0·48	1·750	0·038	1·712

In general, these results show that a high percentage of carbon is accompanied by a high proportion of deposited phosphides, this being especially the case with the first six samples, which represent three different sorts of steel before and after an addition of spiegeleisen (though the contained manganese may also have played some part here). An exception is formed by the "Diamond steel" with 1·17 per cent. of carbon and only 0·028 per cent. of phosphide phosphorus; probably, however, because the total phosphorus in this case was only 0·033 per cent. The burnt iron forms another exception; probably in consequence of an oxidation of hardening carbon, or because the conversion of hardening phosphorus can only occur at a comparatively high temperature and at a very slow rate.

If, therefore, phosphorus seems to favour the deposition of carbide, it would also appear as though, conversely, carbon favours the deposition of phosphorus. Consequently the phe-

nomenon of cold-shortness would not be solely, or to so great an extent, dependent on the amount of hardening phosphorus present. It is necessary to take into consideration at least the total amount of the phosphides and carbides present, or, in other words, the amount of the portion that solidifies last during the cooling of the molten metal, inasmuch as the formation of crystals in the portion of the iron that solidifies first is greatly facilitated as the quantity of the mother metal increases.

E. D. Campbell and S. C. Babcock[1] also distinguish between two different forms of phosphorus in iron and steel. They heated three different sorts of steel to 900–1000° C., and allowed one of each to cool slowly, the others being hardened from various initial temperatures by immersion in water at 4–5° C. Determinations were made of the portion of phosphorus soluble in acid mercuric chloride solution, with the following results:—

Chemical Composition.			Thermal Treatment.	Hardening Temperature, ° C.	Percentage of P Solution in Acid $HgCl_2$.	
C, per cent.	P, per cent.	Mn, per cent.			Percentage of Steel.	Percentage of Total P.
0·10	0·119	0·484	annealed	...	0·099	83·2
,,	,,	,,	hardened	719	0·081	68·08
,,	,,	,,	,,	825	0·079	66·4
,,	,,	,,	,,	928	0·080	67·2
,,	,,	,,	,,	1028	0·086	72·2
0·37	0·160	0·820	annealed	...	0·137	85·6
,,	,,	,,	hardened	728	0·110	68·8
,,	,,	,,	,,	827	0·066	41·2
,,	,,	,,	,,	923	0·048	30·0
,,	,,	,,	,,	1027	0·049	30·6
1·22	0·098	0·780	annealed	...	0·098	100·0
,,	,,	,,	hardened	719	0·087	89·8
,,	,,	,,	,,	750	0·051	52·0
,,	,,	,,	,,	825	0·018	18·3
,,	,,	,,	,,	923	0·015	15·3
,,	,,	,,	,,	1023	0·016	16·2

[1] *Journ. Amer. Chem. Soc.*, vol. xix. pp. 786–790.

An estimate of the molecular weight was made by the author.[1]

C. Sulphur

H. Rocholl reported that the whole of the sulphur is not liberated as sulphuretted hydrogen when cupriferous iron alloys are dissolved in acids; and Fresenius, C. Meinecke,[2] and others found larger or smaller quantities of sulphur in the residues from iron treated with acids; whereas, on the other hand, G. Hattensauer[3] (who found an equal quantity of sulphur from Martin metal, both on oxidising the liberated sulphuretted hydrogen and in the residue left after treatment with concentrated sodium-copper chloride), Craig, F. Brugman,[4] J. O. Arnold, and H. J. Hardy[5] proved the conversion of the total sulphur even in presence of copper.

According to Rocholl,[6] the sulphur in ordinary pig iron and Bessemer iron is converted almost entirely into sulphuretted hydrogen by acids, whereas in cupriferous iron the percentage of sulphur left in the residue increases with the amount of Cu present in the sample.

According to Turner,[7] only a portion of the sulphur in iron containing silicon and sulphur is converted into H_2S by the action of HCl, the rest being retained by the graphitic mass unattacked by this acid. He assumes that sulphur occurs in two modifications in pig iron.

L. Schneider[8] found no sulphur left in the undissolved residue, provided sufficient hydrochloric acid had been used, and the whole boiled half an hour after the evolution of gas had ceased. C. Reinhardt,[9] again, found no ponderable

[1] *Journ. Iron and Steel Inst.*, 1899, vol. i.
[2] *Zeits. f. angew. Chem.*, 1888, p. 376.
[3] *Chem. Ztg.*, xv. p. 521.
[4] *Chem. News*, liv. p. 290.
[5] *Chem. News*, lviii. p. 41.
[6] *Ibid.*, xlvi. p. 236.
[7] *Journ. Iron and Steel Inst.*, 1888, vol. i.
[8] *Oesterr. Zeits. f. Berg- u. Hüttenmesen*, 1898, No. 29.
[9] *Stahl u. Eisen*, 1890, p. 430.

amount of sulphur in the residue left on using HCl of sp. gr. 1·19.

According to L. L. de Koninck,[1] when dilute acids are used, a portion of the sulphur is left in the residue in the form of organic compounds; also, according to W. Schulte and Phillips, a portion of the sulphur is liberated, not as sulphuretted hydrogen, but as $(CH_3)_2S$.

According to Carnot and Goutal,[2] the sulphur appears as MnS when manganese is present; probably, however, FeS, and perhaps also copper sulphide, is likewise present.

D. Chromium

This element occurs in two typical forms in iron—(*a*) distributed (dissolved) in the main mass of the metal, and therefore readily soluble when treated with acids; and (*b*) deposited in the form of acicular crystals, which are attackable only with difficulty by acids. These needles consist of iron-chromium carbides, the composition varying—with the percentage of chromium present. Up to the present, the following have been detected:—

In 50 per cent. ferrochrome, Cr_3FeC_2 (H. Behrens and van Linge; H. von Jüptner).

In chrome steel with about 30 per cent. of chromium, $Cr_2Fe_7C_3$ (H. Behrens and van Linge).

A. Carnot and Goutal[3] have examined ferrochrome of the following composition:—

	I.	II.
Iron	32·6 per cent.	32·2 per cent.
Chromium	57·6 ,,	59·1 ,,
Carbon	9·9 ,,	9·1 ,,

[1] *Loc. cit.* [2] *Compt. rend.*, vol. cxxv. p. 221.
[3] *Ibid.*, vol. cxxvi. pp. 1240–1245.

This they treated with pure hydrochloric acid for two days at 60° C. The insoluble residue was treated with a solution of cadmium- and tungsten borate, and then brought into solution by dissociation with potassium sulphate. The composition corresponded with the formula $Fe_3Cr_9C_7$, which may also be written $Fe_3C . 3Cr_3C_2$. Now Fe_3C is cementite, and Cr_3C_2 is the chromium carbide obtained by Moissan in the electric furnace. According to this, we have to do with either a definite compound or a mixture of these two carbides.

In chrome steel with 2 per cent. and 0·57 per cent. of chromium, they found a carbide of the composition $3Fe_3C . Cr_2C_3$. It would appear as though the carbides of iron and chromium had the power of forming double carbides of divergent composition, the one in ferrochrome containing 3 mols. of chromium carbide to 1 mol. of iron carbide, whilst, on the other hand, the one in chrome steel of low chromium content contains 3 mols. of iron carbide to 1 of chromium carbide.

E. Tungsten

According to Behrens and van Linge, this element is deposited as Fe_2W, or Fe_5W according to Carnot and Goutal.

F. Molybdenum

is deposited in the form of Fe_3Mo_2 in iron alloys, according to Carnot and Goutal.

G. Nickel, Copper, Titanium,

and manganese in excess, seem (according to Carnot and Goutal) to occur dissolved as such in iron, and therefore to be deposited as elements when the metal is dissolved.

H. Oxygen

occurs naturally in iron solely in combination, principally as MnO and FeO, though under certain circumstances SiO_2 may be deposited.

The microscopic appearance, as well as the phenomena of the curves of recalescence, indicate that oxides, like sulphides, are only deposited when the metal has become solid, and at temperatures below 900° C.

According to Carnot and Goutal,[1] the state of combination of S and P in manganiferous steel does not appear to be changed by hardening. Arsenic seems to appear in the free state in steel that has been cooled slowly, whereas hardened steel probably contains Fe_2As.

[1] *Compt. rend.*, 9th July 1900.

CHAPTER X

GASES

LIKE all other liquids, fluid iron is capable of occluding gases; in fact, some gases are also absorbed and retained by the metal when in the solid state. These gases are naturally subject to the general laws of absorption—

1. The solubility of gases in any solvent is proportionate to their pressure (Henry's law, 1803).

2. For all gases that follow Henry's law, by dissolving in proportion to their pressure, the osmotic pressure is equal to the corresponding gas pressure (Van't Hoff).

3. In a mixture of gases, each gas dissolves in accordance with its partial pressure (Dalton, 1807), *i.e.*, when several gases are dissolved together, each exerts the same osmotic pressure as though it were alone.

These laws naturally apply only so long as the gases do not suffer any chemical change in absorption, *i.e.* so long as the molecules have the same composition and dimensions in the free and absorbed state. Otherwise exceptions occur, and it is just these deviations from the laws of absorption that prove the gases to have suffered chemical change during the absorption.

If now we examine the gases occurring in iron alloys, we find them to consist of carbon monoxide, hydrogen, nitrogen (argon), carbon dioxide, and small quantities of oxygen, as the following analyses of the gases enclosed in the bubble cavities show:—

Material.	Method of Preparation.	Volume of Gas.	Composition of Gas.				Observer.
			CO_2.	CO.	H_2.	N_2.	
		c.c.	c.c.	c.c.	c.c.	c.c.	
leisen . .	500 grms. heated to 800° C. *in vacuo*	29·5	...	...	27·0	2·5	Troost and Hautefeuille.
oal pig iron .		16·7	0·6	2·8	12·3	1·0	
d cast steel .		2·20	0·05	1·40	0·50	0·25	
wrought iron							
ding iron) .		18·5	2·2	10·8	4·4	1·1	
teel . .	500 grms. heated to 800° C., first in hydrogen, then *in vacuo*	46·6	...	1·0	44·0	1·5	
oal pig iron .		7·8	...	0·9	6·4	0·5	
wrought iron .		13·9	...	0·6	10·0	3·3	
teel . .	Same treatment, first in CO, then *in vacuo*	16·9	...	14·7	1·5	0·7	
oal pig iron .		3·2	...	2·0	0·8	0·4	
wrought iron .		14·0	...	13·7	0·2	0·1	
IG IRON.							
y I, free from	Broached under water	%	%	%	%	%	Fr. C. G. Müller.
oles . .		3·5	...	3·9	52·1	44·0	
s-Marienhütte		10·0	...	2·8	62·2	35·5	
im (direct from							
t furnace) .		20·0	Experiment miscarried				
om cupola fur-							
(no bubbles)		15·0	...	4·3	86·5	9·2	
om cupola fur-							
(no bubbles)		35·0	...	2·5	83·3	14·2	
rom converter							
r rapid tip-							
) . . .		28·0	...	4·1	81·1	14·8	
OUS SORTS OF L AND IRON.							
mer metal, be- adding spie-	Broached under water						Fr. C. G. Müller.
isen (bubbles)		60·0	...	0·7	88·8	10·5	
mer metal, be- adding spie-							
isen (many							
oles) . .		44·0	...	1·3	80·0	17·9	
mer ingot iron							
ly free from							
oles) (West-							
lia) . .		16·5	...	...	68·0	30·5	
mer rail steel .		48·0	...	...	90·0	9·7	
, ,, .		45·0	...	...	77·0	23·0	
, ,, .		29·0	...	...	76·7	26·3	
steel from							
rali . .		51·0	...	0·9	78·1	20·7	

Material.	Method of Preparation.	Volume of Gas.	Composition of Gas.				Observer.
			CO_2.	CO.	H_2.	N_2.	
VARIOUS SORTS OF STEEL AND IRON—*continued*							
Rail steel (with bubbles), forged	Broached under water.	7·3	...	...	54·9	45·5	Fr. C. G. Müller.
Bessemer spring steel (frothy when cast; a few small bubbles)		21·0	...	...	81·9	18·1	
Martin metal (Bochum) before addition of spiegeleisen		25·0	...	2·2	67·0	30·8	
Dense steel from Bochum (not forged)		17·0	...	1·4	92·4	5·9	
Dense steel from Bochum (forged)		5·5	...	1·3	72·4	25·3	
Mild Thomas steel with 2·5 % of ferromanganese; restless, spurting, swelling moderately, with numerous radial pores		36·0	...	0·6	85·4	14·3	
Basic metal, without addition; quiet in the pot and moulds, slightly spurting, swelling slowly, few radial pores		20·0	...	...	64·5	35·4	
Thomas steel with 5 % of 14 % silicide and 2·5 % of 70 % ferromanganese; steel swelling quietly, block moderately porous		22·0	...	0·4	86·4	12·7	
Thomas steel with 5 % of 14 % silicide; steel swelling quietly, block slightly porous		6·0	...	...	54·7	45·3	
Dense steel	With sharp drill	21	...	1·6	67·1	33·3	Stead.
,, ,,	,, blunt ,,	1100	...	...	88·7	10·3	
Grey pig iron	,, sharp ,,	75	...	?	52·5	44·9	
,, ,,	,, blunt ,,	600	...	?	54·5	45·5	

Zyromski, by annealing different rods of steel in a porcelain tube, obtained the following quantities of gas:—

No.	Material.	Weight of Sample Rod, grms.	Volume of Gas at 15° C. and 750 mm. in c.c.	Percentage Composition.		
				H_2.	CO.	N_2.
1	Ingot iron from Martin furnace, block 240 × 225 mm. . .	24·242	16·00	58·4	5·6	36·0
2	Ingot iron from Martin furnace, block 200 × 195 mm. . .	23·650	18·55	60·9	5·9	33·2
3	Ingot iron from Martin furnace, block 165 × 165 mm. . .	24·450	16·95	52·5	13·5	33·9
4	Ingot iron from Martin furnace, block 70 × 70 mm. . .	24·432	16·80	56·8	6·8	36·4
5	Puddled fine-grained iron, re-heated, faggot rod . .	24·353	16·15	27·8	40·3	31·8
6	Puddled fine-grained iron, not re-heated, billet . . .	23·995	14·10	15·6	45·3	39·0
7	Puddled fine-grained iron, re-heated, faggot rod . .	24·851	16·55	30·8	45·4	23·8
8	Puddled fine-grained iron, not re-heated, billet . . .	23·453	15·25	22·3	45·5	32·1

Müller's investigation of the gases escaping during or shortly after the filling of the mould, gave the following results (tabulated abstract by Dürres):—

[TABLE

Material.	Composition of Material.					Composition of Gas.					Remarks.
	Combined C, per cent.	Graphite, per cent.	Si, per cent.	P, per cent.	Mn, per cent.	CO, per cent.	H_2, per cent.	N_2, per cent.	CO_2, per cent	O_2, per cent.	
A. Pig Iron.											
1. Grey Bessemer pig iron; copious evolution of gas; block dense, fine-grained, grey, with white crust 1 mm. thick .	0·584	3·104	1·68	...	1·93	36·1	55·8	3·6	3·7	0·8	The approximate concordance is attributable to all the different kinds having been fused in a similar furnace atmosphere.
After cal. the oxygen to air, deducting the corresponding N, and re-calculating to 100.	...	...	...	...	...	37·3	58·3	0·5	3·9	...	
2. Spiegeleisen; abundant gas; block dense, flaky, crystalline	4·18	...	0·253	...	7·37	48·1	48·9	2·0	1·2	0·4	
After correction as above .	...	...	...	...	...	48·7	49·5	0·5	1·5	...	
3. Thomas iron; less gas than with 1 and 2. Block free from bubbles, radial . .	3·09	...	0·203	3·025	0·736	37·1	43·7	14·2	3·3	1·2	
Corrected as above . . .	...	...	...	...	...	39·6	46·8	10·0	3·8	...	
B. Bessemer Products.											
4. Rail steel; dense, blown from hot fused charge with moderate Si and Mn content .	0·23 0·28	...	0·15 0·26	0·06 0·08	0·5 0·06	35·5	45·3	11·3	7·0	1·0	
Corrected	...	...	...	...	...	37·3	47·3	7·9	7·5	...	

5. Spring steel; dense (cast from above)	0·48	...	0·15	0·06	0·8	24·1	35·1	29·3	5·9	5·6	
Corrected	0·53	...	0·25	0·08	0·9	34·0	49·5	8·6	7·9	...	
6. The same (poured from below)						41·7	19·1	37·9	0·4	0·7	
Corrected						43·2	19·7	36·7	0·4	...	
7. The same (without further details)						...	...	...	...	...	
Corrected						45·9	41·4	9·9	2·8	...	
8. Rail steel; dense, first mould (corrected)		presumably		same	as 4	38·7	51·3	7·2	2·8	...	
After 17 minutes, last mould (corrected)	...	...	...	...	...	43·4	46·9	6·6	3·1	...	
9. Spring steel; dense, first mould (corrected)		presumably		same	as 5–7	48·2	44·5	2·5	4·8	...	
After 21 minutes, last mould (corrected)	...	...	...	...	...	42·5	36·5	17·1	3·7	...	
10. Rail steel; swelling	?	?	?	?	?	33·0	47·4	10·0	7·6	2·0	
Corrected	...	...	...	...	...	38·4	51·0	2·2	8·4	...	
11. Rail steel; swelling more strongly	?	?	?	?	?	30·2	37·5	23·8	7·4	0·8	The mean composition of the gas differs little from the pig-iron gas.
Corrected	...	...	...	...	...	31·5	39·2	21·6	7·7	...	
12. Rail steel; swelling still more strongly, very restless	?	?	?	?	?	68·6	19·8	9·0	2·0	0·8	
Corrected	...	...	...	...	...	70·7	20·7	6·5	2·1	...	
13. Bessemer steel; completely decarbonised and hot-short, before addition of spiegeleisen. Swelling and copious liberation of gas, zone of worm casts, and single bubbles in centre; first gas sample	?	?	?	?	?	15·6	45·4	33·7	1·8	3·2	Considerable diminution of CO and increase of N.
Corrected	...	...	...	...	...	18·6	54·2	24·9	2·3	...	

Material.	Composition of Material.					Composition of Gas.					Remarks.
	Combined C, per cent.	Graphite, per cent.	Si, per cent.	P, per cent.	Mn, per cent.	CO, per cent.	H_2, per cent.	N_2, per cent.	CO_2, per cent.	O_2, per cent.	
BESSEMER PRODUCTS—*continued*											
14. Bessemer steel completely decarbonised and hot-short, before addition of spiegeleisen. Swelling and copious liberation of gas, zone of worm casts, and single bubbles in centre; second gas sample	?	?	?	?	?	17·5	61·1	29·1	2·2	0·8	Considerable diminution of CO and increase of N.
Corrected	...	...	...	...	...	18·1	52·9	26·8	2·2	...	
15. Martin metal; completely decarbonised, as comparison; first gas sample . . .	?	?	?	?	?	36·50	26·7	30·5	1·3	4·7	Compared with decarbonised Bessemer metal, more CO and less N and H, explained by the protecting cover layer of slag.
Corrected	...	...	...	...	...	48·0	35·1	15·4	1·5	...	
16. Martin metal; completely decarbonised, as comparison; second gas sample . .	?	?	?	?	?	39·0	36·9	17·8	2·9	3·0	
Corrected	...	...	...	...	...	46·0	43·6	6·9	3·4	...	

C. Thomas Products.										
17–22. Thomas metal; soft, prepared with 95 % ferromanganese; no strong spiegel- or ferromanganese reaction; brisk liberation of gas in pots and moulds; poured from below	{0·05 0·10	...	trace	{0·05 0·10	0·45 0·55	...	...	...	...	...
Mean of corrected analyses	...	...	...	...	...	65·0	5·0	30·0	...	...
23. Rail steel; produced by adding 8 % of fused spiegeleisen; strong spiegel reaction	0·25	...	trace	{0·05 0·10	0·45 0·55	67·2	15·8	12·0	4·7	0·3
Corrected	...	...	...	...	...	68·0	16·2	11·0	4·8	...
24. Rail steel; produced by adding 10 % of spiegeleisen; strong spiegel flame; restless product, rapid swelling; gas from above from fourth block; analysis corrected	?	?	?	?	?	56·5	33·0	8·6	1·9	...
25. Rail steel; produced by adding 10 % of speigeleisen; strong spiegel flame; restless product, rapid swelling; gas from above from last block (after 9 minutes); analysis corrected	?	?	?	?	?	62·0	34·2	1·0	2·8	...

Material.	Composition of Material.					Composition of Gas.					Remarks.
	Combined C, per cent.	Graphite, per cent.	Si, per cent.	P, per cent.	Mn, per cent.	CO, per cent.	H_2, per cent.	N_2, per cent.	CO_2, per cent.	O_2, per cent.	
THOMAS PRODUCTS—*continued*											
26. Ingot iron; gas from below, sampling tube removed directly mould was full	...	...	...	...	...	77·9	5·7	14·7	1·7	...	Decrease of CO and increase of H + N definitely confirmed.
Gas from above by means of sand cover, not filled until mould had set; from same mould	...	...	...	...	...	62·6	12·6	23·2	1·6	...	
27. Rail steel similarly treated; first gas sample	...	...	...	...	...	81·7	8·2	9·5	0·6	...	
Second gas sample	...	...	...	...	...	54·1	38·6	3·5	3·8	...	
28. Ingot iron; little gas, completely decarbonised, and before the introduction of reducing agents	...	...	...	...	...	8·0	71·7	18·0	2·0	...	
Corrected	...	...	...	...	...	8·8	71·9	18·1	2·0	...	
29. Ingot iron; gassy, completely decarbonised; first gas sample	...	...	...	...	...	19·3	30·7	41·7	2·1	5·8	Behaviour similar to acid metal.
Corrected	...	...	...	...	...	27·3	43·5	26·2	3·0	...	
Second gas sample	...	...	...	...	...	29·2	32·0	32·0	3·4	3·3	
Corrected	...	...	...	...	...	35·0	38·4	22·5	4·1	...	

30. Ingot iron; prepared with 5 % of 14 % silicide and 2·5 % of 70 % ferromanganese; steel swelling gently, moderately porous (see first table, sample last but one); gas sample from small mould at commencement of pouring .	...	...	...	...	...	58·3	17·0	19·9	1·9	1·8	
Corrected	...	...	...	...	...	64·6	18·9	14·4	2·1	...	
Gas sample from larger mould at end of pouring . .	...	...	...	...	...	36·2	34·1	22·7	3·0	3·7	
Corrected	...	...	...	...	...	44·1	41·6	10·6	3·7	...	
31. Ingot iron; with 5 % of same silicide and 2 % of ferromanganese added red-hot in the pot; no reaction, steel quiet; swelling later with formation of porous zone—											
Before addition . . .	0·002	...	0·002	0·078	0·083	...	...	...	...	...	
After ,, . . .	0·115	...	0·162	0·097	0·944	...	...	...	...	...	
(Calculated)	0·14	...	0·53	...	1·25	...	...	...	...	...	
Gas from one mould . .	...	...	...	...	...	34·7	58·0	4·1	3·2	...	The low N-content is worthy of notice.[1]
Gas from another mould . .	...	...	...	...	...	30·8	65·8	1·9	1·5	...	

[1] Probably displaced by liberated CO.

Material.	Composition of Material.					Composition of Gas.					Remarks.
	Combined C, per cent.	Graphite, per cent.	Si, per cent.	P, per cent.	Mn, per cent.	CO, per cent.	H_2, per cent.	N_2, per cent.	CO_2, per cent.	O_2, per cent.	
BESSEMER PRODUCTS—*continued*											
14. Bessemer steel; completely decarbonised and hot-short, before addition of spiegeleisen. Swelling and copious liberation of gas, zone of worm casts, and single bubbles in centre; second gas sample	?	?	?	?	?	17·5	61·1	29·1	2·2	0·8	Considerable diminution of CO and increase of N.
Corrected	...	...	...	...	...	18·1	52·9	26·8	2·2	...	
15. Martin metal; completely decarbonised, as comparison; first gas sample	?	?	?	?	?	36·50	26·7	30·5	1·3	4·7	Compared with decarbonised Bessemer metal, more CO and less N and H, explained by the protecting cover layer of slag.
Corrected	...	...	...	...	...	48·0	35·1	15·4	1·5	...	
16. Martin metal; completely decarbonised, as comparison; second gas sample	?	?	?	?	?	39·0	36·9	17·8	2·9	3·0	
Corrected	...	...	...	...	...	46·0	43·6	6·9	3·4	...	

C. THOMAS PRODUCTS.																
17–22. Thomas metal; soft, prepared with 95 % ferromanganese; no strong spiegel or ferromanganese reaction; brisk liberation of gas in pots and moulds; poured from below	{0·05 0·10	...	...	trace	{0·05 0·10	0·45 0·55	} ...	...	...	...	...	...	...	...	...	...
Mean of corrected analyses	...	...	...	...	...	...	65·0	5·0	30·0	...	...	...	...	...	...	...
23. Rail steel; produced by adding 8 % of fused spiegeleisen; strong spiegel reaction	0·25	...	...	trace	{0·05 0·10	0·45 0·55	} 67·2	15·8	12·0	4·7	0·3					
Corrected	...	...	...	...	...	...	68·0	16·2	11·0	4·8	...					
24. Rail steel; produced by adding 10 % of spiegeleisen; strong spiegel flame; restless product, rapid swelling; gas from above from fourth block; analysis corrected	?	?	?	?	?	?	56·5	33·0	8·6	1·9	...					
25. Rail steel; produced by adding 10 % of spiegeleisen; strong spiegel flame; restless product, rapid swelling; gas from above from last block (after 9 minutes); analysis corrected	?	?	?	?	?	?	62·0	34·2	1·0	2·8	...					

Material.	Composition of Material.					Composition of Gas.					Remarks.
	Combined C, per cent.	Graphite, per cent.	Si, per cent.	P, per cent.	Mn, per cent.	CO, per cent.	H_2, per cent.	N_2, per cent.	CO_2, per cent.	O_2, per cent.	
THOMAS PRODUCTS—*continued*											
26. Ingot iron; gas from below, sampling tube removed directly mould was full	...	...	...	...	...	77·9	5·7	14·7	1·7	...	Decrease of CO and increase of H + N definitely confirmed.
Gas from above by means of sand cover, not filled until mould had set; from same mould	...	...	...	...	...	62·6	12·6	23·2	1·6	...	
27. Rail steel similarly treated; first gas sample	...	...	...	...	...	81·7	8·2	9·5	0·6	...	
Second gas sample	...	...	...	...	...	54·1	38·6	3·5	3·8	...	
28. Ingot iron; little gas, completely decarbonised, and before the introduction of reducing agents	...	...	...	...	...	8·0	71·7	18·0	2·0	...	
Corrected	...	...	...	...	...	8·8	71·9	18·1	2·0	...	
29. Ingot iron; gassy, completely decarbonised; first gas sample	...	...	...	...	...	19·3	30·7	41·7	2·1	5·8	Behaviour similar to acid metal.
Corrected	...	...	...	...	...	27·3	43·5	26·2	3·0	...	
Second gas sample	...	...	...	...	...	29·2	32·0	32·0	3·4	3·3	
Corrected	...	...	...	...	...	35·0	38·4	22·5	4·1	...	

30. Ingot iron; prepared with 5 % of 14 % silicide and 2·5 % of 70 % ferromanganese; steel swelling gently, moderately porous (see first table, sample last but one); gas sample from small mould at commencement of pouring	...	...	...	...	...	58·3	17·0	19·9	1·9	1·8	
Corrected	...	...	...	...	...	64·6	18·9	14·4	2·1	...	
Gas sample from larger mould at end of pouring	...	...	...	...	...	36·2	34·1	22·7	3·0	3·7	
Corrected	...	...	...	...	...	44·1	41·6	10·6	3·7	...	
31. Ingot iron; with 5 % of same silicide and 2 % of ferromanganese added red-hot in the pot; no reaction, steel quiet; swelling later with formation of porous zone—											
Before addition	0·002	...	0·002	0·078	0·083	...	...	...	...	...	
After ,,	0·115	...	0·162	0·097	0·944	...	...	...	...	...	
(Calculated)	0·14	...	0·53	...	1·25	...	...	...	...	...	
Gas from one mould	...	...	...	...	...	34·7	58·0	4·1	3·2	...	The low N-content is worthy of notice.[1]
Gas from another mould	...	...	...	...	...	30·8	65·8	1·9	1·5	...	

[1] Probably displaced by liberated CO.

From these researches Müller draws the following conclusions:—

1. Molten iron and steel contain a mixture of gas, consisting of CO, H_2, N_2, and CO_2, with small portions of free O_2, the mixture being of very variable composition, and present partly in solution and partly in combination (alloyed).

2. As cooling proceeds, a mixture of these gases is liberated, chiefly consisting of carbon monoxide, together with hydrogen and nitrogen, though fluctuating between certain limits according to the nature and treatment of the iron.

3. The solidified metal retains a quantity of imprisoned gas, which is liberated by broaching, and consists mainly of hydrogen and nitrogen, with a greatly diminished proportion of carbon monoxide.

4. By heating the comminuted metal to redness *in vacuo*, small quantities—to be regarded as combined remainders—of the elementary gases can be driven out and determined.

On comparing the behaviour of the gases absorbed into iron with that of gaseous solutions in water and similar liquids, we find that carbon monoxide, carbon dioxide, and (partly, at least) nitrogen, follow the law of gases. They are also displaced, with comparative ease, from their condition of solution in iron, by other gases; and, according to the above-mentioned researches of Troost and Hautefeuille, it would also appear that the proportion of carbon monoxide at least that can be dissolved varies inversely with the amount of extraneous substances in the iron.

An entirely different behaviour is exhibited by hydrogen, which, indeed, as already mentioned, is almost the only gas present in solid iron (apart from the gases enclosed in the bubble cavities).

Thus Ledebur determined the amount of hydrogen retained by the solid metal (the gas bubbles being as far as possible excluded) by the combustion of the finely

divided samples in dry oxygen, and obtained the following results :—

Ferromanganese with 70 per cent. Mn . . .	0·0028 per cent. by weight.
Ferrosilicon with 11·29 per cent. Si, 2·08 per cent. Mn, and 1·59 per cent. C	0·0028 „ „
Martin iron (poured) with 0·10 per cent. C, 0·14 per cent. Si, and little Mn .	0·0017 „ „

As far back as 1866 Graham found that not only is hydrogen able to diffuse through the metal of a red-hot iron pipe, but also that the metal, when allowed to cool down in an atmosphere of the same gas, occludes 0·46 per cent. of its own volume thereof.[1] Subsequently Cailletet,[2] by electrolysing a solution of ferric chloride, rendered neutral by ammonia, obtained lustrous crystals of iron which were hard enough to scratch glass, and contained 0·028 per cent. of hydrogen. Johnson,[3] Hughes,[4] Baedeker,[5] and Ledebur,[6] showed that iron corroded by dilute sulphuric acid or hydrochloric acid will absorb hydrogen. The author has had occasion to observe that in such cases the hydrogen can diffuse through sheet iron and produce large bubbles in defective places. In these bubbles the gas is contained under considerable pressure.

Roberts-Austen found that the electrolytic precipitation of iron does not always furnish the hard form capable of scratching glass. He gives the breaking strength of electrolytically precipitated iron as 2·7 tons per square inch, increasing to 15½ tons after annealing at 800° C.

The previously cited analyses of the occluded gases show

[1] Graham, *Collected Works*, p. 279.
[2] *Compt. rend.*, lxxx. p. 319.
[3] *Proc. Roy. Soc.*, 1875, xxiii. p. 168.
[4] *Journ. Soc. Telegraph. Eng.*, 1880, p. 163.
[5] *Zeits. d. Ver. deutsch. Ing.*, 1888, p. 186.
[6] *Stahl u. Eisen*, 1887, p. 681 ; 1889, p. 745.

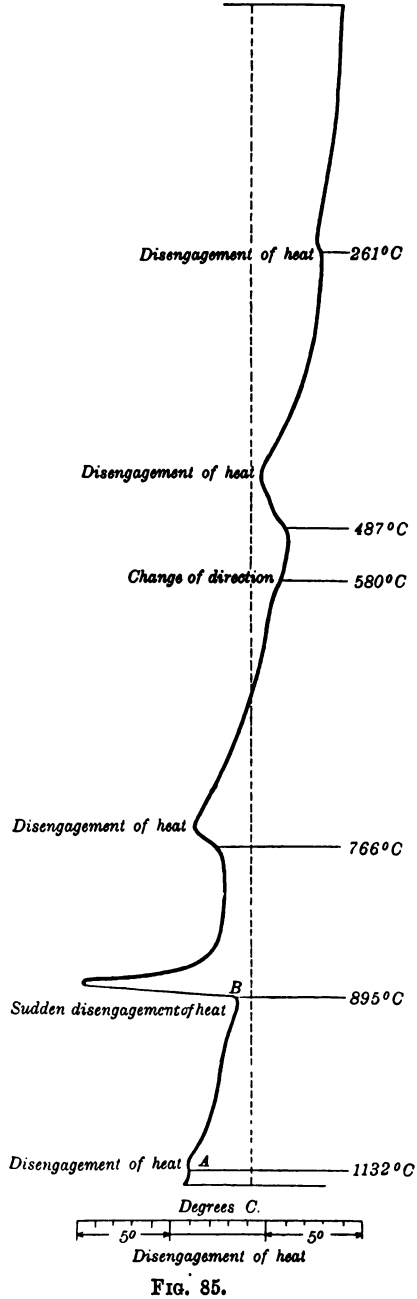


FIG. 85.

that Bessemer steel in the solid state contains far more hydrogen than nitrogen or carbon monoxide, although in the converter the metal is traversed by powerful currents of air containing only a relatively small proportion of water vapour.

Special interest attaches to the latest researches of Roberts-Austen.[1] By galvanic precipitation of a carefully prepared, chemically pure solution of ferric chloride, he produced a piece of pure iron 5 grms. in weight; this was rather harder than fluorspar, and, when warmed in water at 70° C., disengaged hydrogen, the evolution of gas ceasing after several hours. The iron was inserted in a porcelain tube, which was then evacuated by means of a

[1] *Fifth Report to the Alloys Research Committee of the Inst. of Mech. Eng.*, 1899.

mercury air-pump, and heated, whereupon a further evolution of hydrogen was obtained. Although this disengagement of gas never entirely ceased, it was nevertheless very slight indeed by the time the temperature of 1300° C. was attained.

Fig. 85 represents the cooling curve of this metal after being four times heated, and shows that the same contains at least three hitherto undetected critical points. The co-ordinates are, as usual, time and temperature; the latter, however, does not represent the actual temperature of the metal, but to a large extent the disengagement of heat at the temperatures given below.

The critical points observed are the following:—The point A, at 1130° C., which had already been observed by Dr. E. J. Ball; also B, corresponding to the ordinary point Ar_3 of Osmond, at 895° C. In the course of further cooling, the point Ar_2 appears at 770° C. Ar_1 is absent. On the other hand, a disengagement of heat recurs at between 550° and 600° C., though its precise position is difficult to define, as it seems to vary a little on the repetition of the experiments. The next critical point is one of extreme interest. It occurs between 450° and 500° C., and appears to be connected with the retention of hydrogen by the iron—even though heated to 1300° C. Finally, another critical point appears at 270° C. (*i.e.* 400° C. below red heat).

These researches throw a new light on the relation between iron and hydrogen. The two lowest of the critical points mentioned appear even after the electrolytically precipitated iron has been heated *in vacuo* three times in succession to 1300° C.; however, on frequently repeating this heating *in vacuo*, they become so faint as to be difficult of identification. There is therefore little doubt but that they are caused by the presence of occluded hydrogen. The higher of these points might correspond with the deposition of an

iron hydride from the solid solution, the lower one (at 270° C.), however, to the appropriate eutectic solution.

It is worthy of note that the amount of heat liberated by electrolytically precipitated iron at all the critical points, except the lowest, is diminished by repeated heating *in vacuo*, but can be restored to the original figure by re-saturating the metal with hydrogen (employing the iron to serve as negative electrode in the decomposition of acidified water). These results, which indicate that the molecular changes of condition of iron depend on, or are at least influenced by, the presence of small quantities of hydrogen, entail further careful investigation. Other researches of Austen's, still uncompleted, indicate that the relations between iron and hydrogen are far more complex than was believed.

Mention must here be made of the noteworthy circumstance that it is just the tetravalent metals of Mendelejeff's group VIII. (namely, iron, cobalt, nickel, ruthenium, rhodium, palladium and osmium, iridium, platinum) that exhibit a special affinity for hydrogen.

Nitrogen, also, is tenaciously retained in small quantities by iron; the researches on this point, however, are so incomplete, and the influence of nitrogen on the properties of the metal so slight, that mere mention must suffice. Furthermore, the fact that iron forms with carbon monoxide a definite chemical compound of ready volatility need only be referred to in passing.

BOOK IV

THE CHEMICAL COMPOSITION OF SLAG

CHAPTER I

INTRODUCTORY

THE mutual reactions occurring between slag and metal constitute one of the most important factors in the majority of metallurgical processes. Later on we shall have occasion to go into this matter more fully, but will now proceed to deal with the chemical composition of slag, so that afterwards we can revert thereto.

A. Ledebur was the first to regard slags as solutions, instead of complex chemical compounds. On this point he says:[1]—

"All the constituents of slags, and especially the oxides mentioned,[2] of which the slags mainly consist, appear in extremely fluctuating mutual proportions, and without reference to stöchiometric ratios. Hence it follows, in the first place, that a slag is not necessarily a single chemical compound (*e.g.* a silicate of definite formula), but should be regarded as a solidified solution of various chemical compounds in one another. That these compounds mainly consist of

[1] *Handbuch der Eisenhüttenkunde*, 2nd edition, i. p. 175.

[2] Oxides of metals, silicon, phosphorus, etc.

oxygen compounds of the metals and metalloids has already been mentioned."

He also says:[1]—

"Borax and phosphate in a molten condition form excellent solvents for a very large number of oxides, and solidify therewith to 'glasses' of homogeneous composition, no matter what the mutual proportions by weight. There is no reason to suppose that, when silica or phosphoric acid are brought into association with lime, magnesia, ferrous oxide or other substances at high temperatures, the formation of a simple mutual solution of the bodies is impossible, and that much closer combination must necessarily occur.

"Of course there is no doubt but that certain combinations can occur within a solution, and therefore also within a liquid slag, though, to be sure, these combinations do not come into decided evidence until solidification is proceeding, or is complete."

How accurate are these opinions of Ledebur we shall see hereafter.

To facilitate the study of the chemical composition of slags, we will divide them into three groups, viz.—

1. Silicate slags, consisting of metallic oxides and silica.

2. Phosphatic slags, consisting of metallic oxides and phosphoric acid. They occur solely in admixture with silicate and oxide slags.

3. Oxide slags, consisting solely of metallic oxides. These, also, are not met with pure in practice.

[1] *Loc. cit.* p. 176.

CHAPTER II

SILICATE SLAGS

BEFORE proceeding to describe the silicate slags, we will first make the acquaintance of the various existing hydrates of silica.

Of all the possible forms, only ortho- (H_4SiO_4) and meta-silicic acid (H_2SiO_3) are known in the free state. They furnish numerous other pyro- or poly-silicic acids on hydrolysis (*e.g.* di-silicic acid, $H_2Si_2O_5$, and tri-silicic acid, $H_4Si_3O_8$), but these are not known in an uncombined condition, though many of the corresponding silicates are found as minerals.

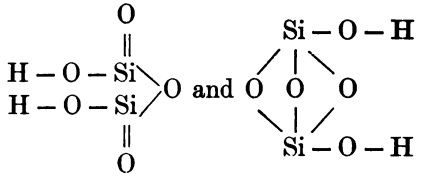
The subjoined table (chiefly after Weltzien) shows all the theoretically possible varieties of silicic acid.

Name.		Mono-	Di-	Tri-	Poly-
		Silicic Acids.			
2 basic or meta-	Silicic Acid.	H_2SiO_3	$H_2Si_2O_5$	$H_2Si_3O_7$	$H_2Si_mO_{2m+1}$
4 ,, ,, ortho-		H_4SiO_4	$H_4Si_2O_6$	$H_4Si_3O_8$	$H_4Si_mO_{2m+2}$
6 ,, . .		H_6SiO_5	$H_6Si_2O_7$	$H_6Si_3O_9$	$H_6Si_mO_{2m+3}$
8 ,, . .		H_8SiO_6	$H_8Si_2O_8$ [1]	$H_8Si_3O_{10}$	$H_8Si_mO_{2m+4}$
10 ,, . .		$H_{10}SiO_7$	$H_{10}Si_2O_9$	$H_{10}Si_3O_{11}$	$H_{10}Si_mO_{2m+5}$
12 ,, . .		$H_{12}SiO_8$	$H_{12}Si_2O_{10}$	$H_{12}Si_3O_{12}$ [2]	$H_{12}Si_mO_{2m+6}$
$2n$,, . .		$H_{2n}SiO_{n+2}$	$H_{2n}Si_2O_{n+4}$	$H_{2n}Si_3O_{n+6}$	$H_{2n}Si_mO_{2m+n}$

The formula in italics is the general formula for silicic acid, which, however, only has an actual value when both n

[1] Impossible, since it is only $2(H_4SiO_4)$.
[2] Impossible, since it is only $3(H_4SiO_4)$.

and m are greater than zero. Of course one can also imagine the occurrence of isomers among the silicic acids, *e.g.*—



and also that certain of these will merely represent a plurality of molecules of simple hydrated silica. This latter event *may* ensue when the formula of a polysilicic acid is a multiple of a more simple one; it *must* occur when the formula is a multiple of an ortho-silicic acid.

The silicates, also, can be divided in accordance with this scheme, and we thus obtain, for example, meta-mono-silicates, ortho-di-silicates, hexabasic tri-silicates, etc.

In metallurgy, however, a different nomenclature is generally employed, as is shown in the appended table, along with the corresponding older chemical names.

Oxygen Ratio. Acid / Base.	Older Chemical Name.	Metallurgical Nomenclature.	Molecular Formula for—	
			Monoxide Bases.	Sesquioxide Bases.
1 : $1\frac{1}{2}$	$\frac{1}{3}$-silicate	Sub-silicate	$\dot{R}_3SiO_5$	$\ddot{R}_2SiO_5$
1 : 1	$\frac{1}{2}$- ,,	Singulo- ,,	$\dot{R}_2SiO_4$	$\ddot{R}_4Si_3O_{12}$
$1\frac{1}{2}$: 1	$\frac{3}{4}$- ,,	Sesqui- ,,	$\dot{R}_4Si_3O_{10}$	$\ddot{R}_8Si_9O_{30}$
2 : 1	mono- ,,	Bi- ,,	$\dot{R}SiO_3$	$\ddot{R}_2Si_3O_9$
3 : 1	$1\frac{1}{2}$- ,,	Tri- ,,	$\dot{R}_2Si_3O_8$	$\ddot{R}_4Si_9O_{24}$

In order to obtain further information on the constitution of the silicate slags, we may now make use of the fusing-point curves and the microscopical examination.

With regard to the latter, it should now be mentioned, once for all, that amphibole minerals, felspar minerals, free

acids, and free sesquioxides, are never found in slags. The first named have never been prepared by mineral synthesis (fusion); the occurrence of alkali-felspar is impossible on account of deficiency of alkali; and melilite or gehlenite always appears in place of anorthite and labrodorite.

Consequently the presence of free sesquioxides and free silicic acids as constituents of silicate slags is *primâ facie* impossible.

No fusing-point curves have as yet been compiled for slags; and in fact, as the following table will show, the existing reports on the fusing temperatures and temperatures of formation of slags are very defective:—

A. Temperatures determined with Princep's Alloys.

Substance.	Temperature of Formation.	Fusing Point.
	°C.	°C.
Glass (plumbiferous)	...	1000 (1400)
Glass (leadless)	...	1200
Slag from ore smelting at Muldener-Hütte	...	1030
Similar slag, very rich in zinc oxide	...	1030
(Both slags were full of bubbles when cold. Complete fusion does not seem to occur below 1130°C.)		
Copper-ore concentration slag	...	1045
Melaphyr from Mulatto	...	1106
Pitchstone from Arrau	...	1106
Hauyn basalt from Neudorf, near Annaberg	...	1080–1106
Leucite basalt from Pöhlberg, near Annaberg	...	1130
Syenite from Edle Krone, near Tharandt	...	1130–1160
Pitchstone porphyry from Leisnig	...	1130–1160
Quartz porphyry from the Travigno Valley	...	1130–1160
Asbestos, about	...	1300
Regulus slag from the old Freiberg method	...	1160–1178
Pure Altenberg zinc slag	...	1160
Copper	...	1100
29·1 SiO_2 + 70·9 BaO	1444	...
37·6 ,, + 62·4 ,,		...
52·0 ,, + 48·0 CaO		...
61·8 ,, + 38·2 ,,		...
59·8 ,, + 40·2 MgO		...
69·0 ,, + 31·0 ,,		...
64·3 ,, + 35·7 Al_2O_3		...
73·0 ,, + 27·0 ,,		...
Blast-furnace slag: 50% SiO_2, 17% Al_2O_3, 3% FeO, and 30% CaO	1392	1208
Freiberg regulus slag: 48% SiO_2, 9% Al_2O_3, 37% FeO, 4·5% CaO, 1·5% MgO	1326	1166

given by Akerman to be otherwise than at least similar to the fusing-point curves.

D. TEMPERATURES OF FORMATION AND FUSION OF SINGULO-SILICATE SLAGS, CALCULATED—(*a*) AFTER P. GREDT, (*b*) AFTER R. AKERMAN.[1]

a			*b*					
No.	Oxygen ratio, $\frac{Al_2O_3}{CaO}$.	Temperature of Formation of the Slag.	Oxygen Ratio, $\frac{Al_2O_3}{CaO}$.	Total Heat of Fusion per Unit Weight of Slag.	Calculated Temperature of Fusion based on the Specific Heat given.			
					Assumed Specific Heat.	Calculated Fusing Points.	Assumed Specific Heat.[2]	Calculated Fusing Points.
		°C.		Calories.		°C.		°C.
1	0·00	1570	...	...	...	...	...	...
2	0·05	1526	...	...	...	...	...	...
3	0·11	1492	...	...	...	...	...	...
4	0·18	1468	...	...	...	...	...	...
...	...	...	0·20	428	0·30	1427	0·320	1338
5	0·25	1451	2·25	410	0·30	1367	0·312	1314
...	...	...	0·30	380	0·30	1267	0·305	1246
6	0·33	1439	...	...	...	...	...	...
...	...	...	0·40	363	0·30	1210	0·299	1215
7	0·43	1430	...	...	...	...	...	...
...	...	...	0·50	349	0·30	1163	0·291	1199
8	0·54	1422	...	...	...	...	...	...
9	0·67	1417	...	...	...	...	...	...
...	...	...	0·70	347	0·30	1157	0·290	1197
10	0·81	1412	...	...	...	...	...	...
...	...	...	0·90	355	0·30	1183	0·296	1200
11	1·00	1410	1·00	361	0·30	1203	0·299	1207
...	...	...	1·20	377	0·30	1257	0·305	1236
12	1·22	1430	...	...	...	...	...	...
13	1·50	1468	1·50	400	0·30	1333	0·310	1290
14	1·86	1526	...	...	...	...	...	...
...	...	...	2·00	430	0·30	1433	0·320	1344
15	2·33	1613	...	...	...	...	...	...
...	...	...	2·35	461	0·30	1537	0·327	1410

Figs. 86–89, Plate X., give the total heats of fusion of different silicates of lime, or lime and magnesia, from the monosilicate to the tri- and tetra-silicate. They are exactly similar to the freezing-point curves of solutions.

[1] *Jernkont. Ann.*, 1889, Nos. 5 and 6; *Stahl u. Eisen*, 1890, p. 424.

[2] According to Akerman's observations, these specific heats vary between 0·29 and 0·33, and are lower with fusible than for refractory slags.

Fig. 90.

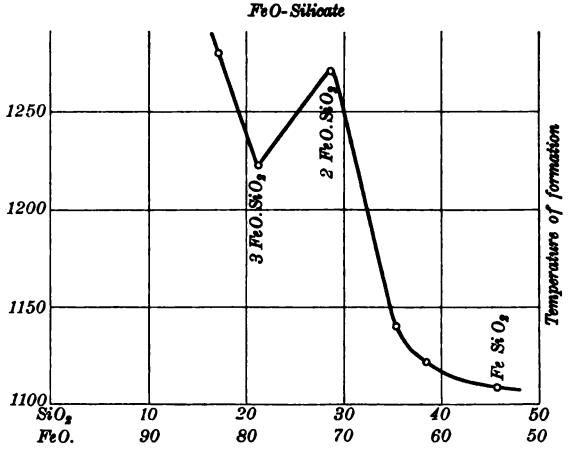
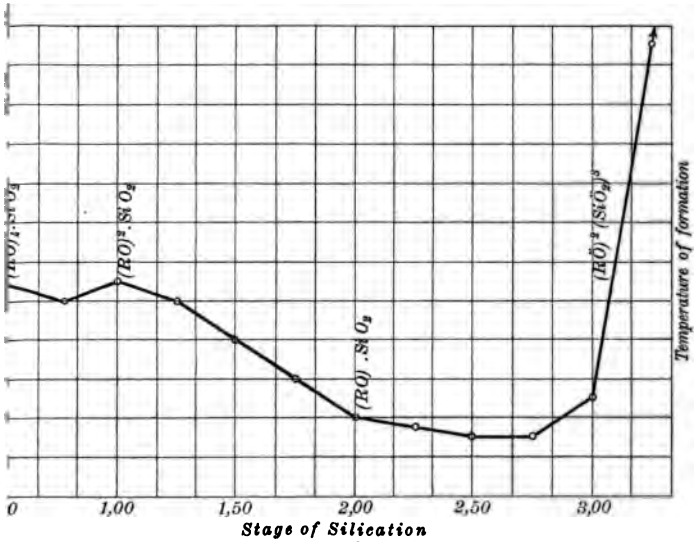
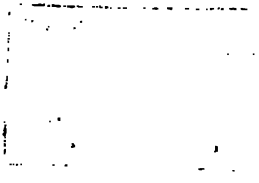


Fig. 91.



$F_2O : CaO = 2 : 1$ $(RO = {}^2/_3\ FeO\ {}^1/_3\ CaO)$



These curves give two minima for each series of silicates, namely—

	1st Minimum.	2nd Minimum.
CaO = silicate . . .	1·5 = silicate	2·83 = silicate
$(3CaO + MgO)$ = silicate .	1·5 = „	2·5 = „
$(2CaO + MgO)$ = „ .	1·5 = „	2·39 = „
$(CaO + MgO)$ = „ .	1·5 = „	2·7 = „

and three maxima, the central one of which corresponds—

with CaO = silicate . . .	to the 1·87 = silicate
„ $(3CaO + MgO)$ = silicate . .	„ 1·76 = „
„ $(2CaO + MgO)$ = „ . .	„ 1·78 = „
„ $(CaO + MgO)$ = „ . .	„ 1·76 = „

Similar curves are given in Figs. 90 and 91 for FeO-silicates and iron-calcium silicates (according to H. O. Hofman).[1] These need no further explanation.

In this way one of the constituents of the solution would be revealed as a metasilicate, whilst the two minima to the right and left of these maxima must correspond to the solidification points of eutectic mixtures.

The occurrence of metasilicates in slags was presumable, since this hydrate is known in the free state. Furthermore, Vogt[2] has proved the presence, in slags, of a whole series of metasilicates, (enstatite, $MgSiO_3$; hypersthene and bronzite, $(FeMg)SiO_3$; wollastonite, $CaSiO_3$; augite, $Ca(Mg,Fe)SiO_3$; rhodonite, $MnSiO_3$; babingtonite, $n(Mn,R)SiO_3 + Fe_2Si_3O_9$; a new hexagonal calcium silicate ($CaSiO_3$)).[3] Now, what are the compounds appearing in addition to these in the two eutectic mixtures? They cannot be free sesquioxide bases and free silicic acids, since we have already seen that these do not occur at all in slags; consequently the bodies in question must be silicates.

[1] The temperatures at which certain ferrous and calcic silicates are formed in fusion (*Trans. Amer. Inst. Ming. Eng.*, Sept. 1899).

[2] "Studier over Slagger," *Bihang t. k. svenska Vet. Akad. Handlingar*, vol. ix., No. 1; "Om Slaggers af Sammansättningen beroende kristallisationsförhallanden," *Jernkont. Ann.*, 1885; *Beiträge zur Kenntnis der Mineralbildung in Schmelzmassen*, Christiania, 1892.

[3] See also in Book II.

As the more basic compound, the orthosilicate seems the more probable, since this acid is also known in the free state, and because Vogt also found similar silicates (olivine, $(Mg,Fe)_2SiO_4$; fayalite, $(Mn,Fe)_2SiO_4$; thephroite, Mn_2SiO_4; monticellite, $CaMgSiO_4$; melilite, $(RO)_{12}(Al_2O_3)_2(SiO_2)_9$; willemite, Zn_2SiO_4).

A more difficult question to answer is that respecting the acid constituents of the mixture, since Vogt mentions only one acid silicate $(RO_2)(SiO_2)_3$, which occurs as globulites or crystallites in siliceous enamel slags (of a stage of silication equal to at least 2·5). On the other hand, the heat-of-fusion curve of the calcium silicates (Fig. 86) extends as far as the tetrasilicate without revealing any decided maximum, so that, at the most, only the salts of di-silicic acid ($H_2Si_2O_5$) or the di-basic tri-silicic acid ($H_2Si_3O_7$) can be in question.

In slags with an oxygen ratio, 0·5–0·8, Vogt detected a mineral, gehlenite, which corresponds to a 0·67 silicate.

We thus have as constituents of slag—

Stage of Silication.	Typical Formula.	Mineral.	
0·67	$\ddot{R}_3SiO_5$	Gehlenite $(RO)_3.(Al_2O_3).(SiO_2)_2$	Tetragonal
1·00	$\ddot{R}_2SiO_4$	Melilite $(RO)_{12}.(Al_2O_3)_2(SiO_2)_9$	,,
,,	,,	Olivine $(MgO)_2.SiO_2$	Rhombic
,,	,,	Fayalite $(FeO)_2.SiO_2$	,,
,,	,,	Tephroite $(MnO)_2.SiO_2$	,,
,,	,,	Monticellite, $CaO.MgO.SiO_2$	,,
,,	,,	Willemite $(ZnO)_2.SiO_2$	,,
1·50	$\ddot{R}_4Si_3O_{10}$	New non-aluminous, calcareous, tetragonal mineral: akermanite $(R_4Si_3O_{10})$.	
2·00	$\ddot{R}SiO_3$	Hexagonal calcium silicate, $CaSiO_3$	Hexagonal
,,	,,	Wollastonite, $CaSiO_3$	Mono-symmetrical
,,	,,	Augite varieties, $Ca(Mg)SiO_3$	,,
,,	,,	Rhodonite, $MnSiO_3$	Asymmetrical
,,	,,	Babingtonite, $n(Mn, R)SiO_3 + Fe_2Si_3O_9$	,,
,,	,,	Enstatite, $MgSiO_3$	Rhombic
,,	,,	Hypersthene, Bronzite } $(Fe,Mg)SiO_3$	,,
,,	,,		
3·00 (?)	$\ddot{R}_2Si_3O_8$ (?)	Globulites in acid enamel slags.	
4·00 (?)	$\ddot{R}Si_2O_5$	?	
6·00 (?)	$\ddot{R}Si_3O_7$	?	

The last three members are more or less hypothetical.

There now only remains to be mentioned the relation between the appearance of these minerals and the composition of the slag; and in this connection we have mainly to depend on the researches of Vogt. He says on this point:—

"A comparative examination of the analyses shows that the formation of minerals in the molten mass chiefly depends on the chemical composition of the average mass, the minerals being products of the chemical affinity of the predominating constituents (or, in other words, the formation of minerals is based on chemical mass reactions). The divergent physical conditions possible in the formation of slags exert only a minimum secondary influence on the reaction, provided a certain minimum limit be not exceeded for the period of crystallisation." [1]

In strong enamel slags, rich in silica (2·5 per cent.-silicates), there occur, according to Vogt, as already mentioned, globulites and crystallites of a silicate probably corresponding to the formula $(\ddot{R}O)_2 . (SiO_2)_3$.[2]

Enstatite crystallises out from the di-silicate slags, provided the molten mass contains more MgO(+FeO) in proportion to CaO(+MnO) than corresponds to the molecular ratio 2·44MgO : 1CaO; on the other hand, augite is formed when the CaO exceeds the ratio 1·40MgO : 1CaO. Should the lime content be in excess of 0·3MgO : 1CaO, wollastonite, or the new hexagonal lime silicate, is formed. (The former probably in the more siliceous slags, the latter in those poorer in silica.) Rhodonite is formed in di-silicate slag when the proportion of MnO to RO(=CaO, MgO, FeO) is greater than 1MnO : 0·9RO; but augite forms, when the manganese content falls below the ratio, 1MnO : 7RO with a

[1] In the case of non-aluminous minerals, *e.g.* the new tetragonal mineral (if the melt be free from alumina), this amounts to only a few minutes (5–7 at most); on the other hand, several hours to days are needed for aluminous minerals in strongly aluminous melts.

[2] RO = CaO and MgO.

medium content of MnO; *e.g.* 1MnO : 1·82RO, both rhodonite and augite, may be formed at the same time.

When the composition of the slag approximately corresponds to singulo-silicate, olivine is always formed if there be more RO(= MgO, MnO, FeO) in proportion to CaO (together with Na_2,OK_2O) than corresponds to the ratio 1RO : 1·10–1·20CaO.[1]

Melilite, or one of the other tetragonal minerals, is formed, on the other hand, when the lime content is higher than the ratio RO : 1·25–1·30CaO.[2] In the intervals between these two limits, both adjacent minerals may be formed.

The pyroxene minerals with the hexagonal lime silicate are only deposited from slags that contain more silica than corresponds to the oxygen ratio $\frac{\text{acid oxygen}}{\text{basic oxygen}} = 1{\cdot}50–1{\cdot}60$.[3] The line of demarcation between the slags containing the hexagonal lime silicate and one of the tetragonal minerals appears to be located precisely at the stage 1·42–1·45 of silication; the boundary between the augite slags and those containing tetragonal minerals, at the stage of silication, 1·50–1·53; whilst that between the augite and enstatite slags and the olivine slags is at 1·55. The presence of more or less alumina appears to have little influence on the foregoing limits.

The position occupied in the group of tetragonal minerals by the new member, comparatively rich in silica and CaO, is between the oxygen ratios 1·35–1·50 (presumably only when little alumina is present) and gehlenite only when the slag is at once strongly basic (less than 0·8 per cent. of silicates) and rich in alumina. The true melilite lies in the interval between the two.

[1] The former limit applies to a high content of alumina (about 20 per cent.), the latter for a percentage of about 3 per cent.

[2] The limit varies according to the percentage of alumina.

[3] Al_2O_3 reckoned as base.

The earlier assumption that the various maxima in the heat of fusion correspond to the above-mentioned silicates, finds a remarkable confirmation in the graphical representation of the foregoing mineralogical composition of slags (Fig. 90). Our maximum temperatures coincide throughout with the middle of the mineralogical groups there indicated: thus, for di-silicates, in the augite and enstatite group,[1] for monosilicates in the melilite and olivine group. In slags rich in CaO there seems to be also a maximum somewhere near the sub-silicates in the gehlenite group.

In conclusion, it is advisable to mention some more basic silicates than those hitherto described, although they really belong to the oxide slags.

Refinery slags consist of fayalite, magnetite, and an excess of FeO. The very basic slags are characterised throughout by a high content of sesquioxides. Thus, for example, spinel, $RO.R_2O_3$, which invariably crystallises out earlier than the silicate minerals, appears only when the silica content is very low (to singulo-silicate), and the alumina and magnesia relatively high. Spinel sometimes contains only MgO, at others also CaO; ZnO-spinel forms more readily than MgO-spinel.

In charges containing FeO and Fe_2O_3 at the same time, magnetite is readily formed when the slag itself contains silica (though it must not be more acid than di-silicate). In slags containing spinel the deposition of magnetite succeeds that of this mineral, but precedes or accompanies the separation of the silicate minerals. Ferric oxide also readily combines with other RO bases.

According to the researches of L. Bourgeois, MnO can also readily combine with Al_2O_3, or with Mn_2O_3.

[1] Both the calcium silicates have the same composition, and can therefore be classified in the one group.

Provided the cooling be effected very quickly, an excess of alumina prevents crystallisation (though perhaps not in very basic masses), and therefore produces vitreous slags.

Sulphide in slag invariably appears as a monosulphide (CaS, MnS, FeS, and isomorphous mixtures of these) or regular crystalline habit; in highly basic enamel slags these compounds appear as globulites.

Hence, in very basic slags, the sesquioxide compounds —together with excess RO-bases—seem to predominate.

CHAPTER III

CALCULATING THE COMPOSITION OF SILICATE SLAGS

AN approximate calculation of the composition of slags can be made on the basis of the graphical table given in Fig. 90. A commencement is made with the oxygen of the silica, as well as all the bases (except Cu_2O, which seems to have practically no affinity for silica); then from the sum of the latter is deducted one-half of the sulphur content (corresponding to the oxygen equivalent of the RS), and from this result is calculated the ratio $\frac{\text{acid oxygen}}{\text{basic oxygen}}$: from this the composition of the slag can approximately be determined, *i.e.* the components of the mixture can be estimated.

Should the oxygen ratio exceed 2·0, then the slag will consist of the silicates RSi_2O_3 and $R_2Si_3O_8$ (probably), or expressed in rational formulæ: $RO \,.\, SiO_2$ and $(RO)_2(SiO_2)_3$, and we may state the composition as—

$$x\text{RO} \,.\, SiO_2 + y(RO)_2(SiO_2)_3.$$

By then indicating the oxygen of the silica by s, and that of the bases by b, we have—

$$2x + 6y = s$$

and—

$$x + 2y = b.$$

This gives—

$$y = \frac{s}{2} - b$$

and—

$$x = 3b - s.$$

EXAMPLE.

Take a slag of the following composition:—

	Per cent.		Per cent.	
SiO_2	61·16	containing oxygen	**32·62** $= s$	
Al_2O_3	4·43	„ „	2·05	
CaO	22·83	„ „	6·52	
MgO	10·25	„ „	4·10	**13·07** $= b$
MnO	0·49	„ „	0·11	
FeO	1·28	„ „	0·28	
Total	100·44			

$$\frac{\text{Acid oxygen}}{\text{Basic oxygen}} = \frac{32{\cdot}62}{13{\cdot}07} = 2{\cdot}49$$

$$y = \frac{s}{2} - b = 16{\cdot}31 - 13{\cdot}07 = 3{\cdot}24$$

$$x = 3b - s = 39{\cdot}21 - 32{\cdot}62 = 6{\cdot}59.$$

The formula expressing the composition is therefore—

$$= 6{\cdot}59\text{RO} \,.\, SiO_2 + 3{\cdot}24(\text{RO})_2(SiO_2)_3.$$

Similarly, we have, for a slag intermediate between di-silicate and the singulo-silicate, the formula—

$$x\text{RSiO}_3 + y\text{R}_2\text{SiO}_4$$

or— $$x\text{RO} \,.\, SiO_2 + y(\text{RO})_2(SiO_2),$$

and further— $$2x + 2y = s$$

$$x + 2y = b,$$

whence follows— $$x = s - b$$

$$y = b - \frac{s}{2}.$$

EXAMPLE.—*Composition of Slag.*

	Per cent.		Per cent.	
SiO_2	47·87	containing oxygen	**25·53** $= s$	
Al_2O_3	5·37	„ „	2·50	
CaO	37·76	„ „	10·79	
MgO	7·78	„ „	3·11	**16·64** $= b$
MnO	0·37	„ „	0·08	
FeO	0·72	„ „	0·16	
Total	99·87			

$$\frac{\text{Acid oxygen}}{\text{Basic oxygen}} = \frac{25{\cdot}53}{16{\cdot}64} = 1{\cdot}53$$

$$x = s - b = 25{\cdot}53 - 16{\cdot}64 = 8{\cdot}89$$

$$y = b - \frac{s}{2} = 16{\cdot}64 - 12{\cdot}76 = 3{\cdot}88.$$

Hence the formula is $8{\cdot}89RSiO_3 + 3{\cdot}88R_2SiO_4$.

In the case of slags with an oxygen ratio of less than 1·0, and rich in MgO and Al_2O_3, as well as in di-silicate slags containing Fe_2O_3, another method of calculation (to be described later) is adopted.

When the oxygen ratio is between 1·0 and 0·5, and there is not more than 0·7 (MgO + MnO + FeO) to 1CaO, we have— $x(RO)_3 . SiO_2 + y(RO)_2 . SiO_2$,

and hence— $2x + 2y = s$

$3x + 2y = b$,

whence follow— $x = b - s$

$$y = \frac{3}{2}s - b.$$

EXAMPLE.—*Composition of Slag.*

	Per cent.		Per cent.	
SiO_2	28·32	containing oxygen	**15·10** = s	
Al_2O_3	24·24	„ „	11·30	
CaO	40·12	„ „	11·46	
MgO	2·79	„ „	1·12	**23·96** = b
MnO	0·07	„ „	0·02	
FeO	0·27	„ „	0·06	
CaS	3·38			

$$\frac{\text{Acid oxygen}}{\text{Basic oxygen}} = \frac{15{\cdot}10}{23{\cdot}96} = 0{\cdot}63$$

$$x = b - s = 23{\cdot}96 - 15{\cdot}10 = 8{\cdot}86$$

$$y = \frac{3}{2}s - b = 22{\cdot}65 - 23{\cdot}96 = -1{\cdot}31.$$

We obtain for y a small but negative value, which is evidently an impossibility, but indicates that this slag

mainly consists of gehlenite, though spinel is certainly also present.

The amount of spinel ($RO . Al_2O_3$) can be calculated as follows:—

As we have seen, this slag can only consist of gehlenite and spinel. If we represent the basic oxygen in gehlenite by b_1, then evidently $\frac{s}{b_1} = 0{\cdot}67$, and from this the basic oxygen in the gehlenite works out to—

$$b_1 = \frac{s}{0{\cdot}67} = \frac{15{\cdot}10}{0{\cdot}67} = 22{\cdot}53.$$

Consequently the oxygen content of the spinel is—

$$b - b_1 = 23{\cdot}96 - 22{\cdot}53 = 1{\cdot}43,$$

and since this mineral ($RO . Al_2O_3$) contains 4 oxygen atoms to the molecule—

$$\text{spinel } (RO,Al_2O_3) = \frac{b - b_1}{4} = 0{\cdot}35,$$

whilst of gehlenite we find—

$$x = \frac{s}{2} = 7{\cdot}55.$$

The composition of the slag is therefore expressed by—

$$7{\cdot}55(RO)_3 . SiO_2 + 0{\cdot}35RO . Al_2O_3.$$

With oxygen ratios below 1·0, and with over 0·7 ($MgO + MnO + FeO$) to 1 CaO, we are in presence of a mixture of olivine and spinel, and therefore have—

$$x(RO)_2SiO_2 + yRO . Al_2O_3,$$

and further— $2x = s$

$$2x + 4y = b,$$

hence— $x = \frac{s}{2}$

$$y = \frac{b - s}{4}.$$

EXAMPLE.

	Per cent.		Per cent.	
SiO_2 . .	24·40	containing oxygen	**13·00**	$= s$
Al_2O_3 . .	4·90	,, ,,	2·30	
CaO . .	0·53	,, ,,	0·15	
MgO . .	trace	,, ,,	trace	**17·37** $= b$
MnO . .	0·13	,, ,,	0·04	
FeO . .	66·94	,, ,,	14·88	

$$\frac{\text{Acid oxygen}}{\text{Basic oxygen}} = 0{\cdot}75$$

$$x = \frac{s}{2} = \frac{13{\cdot}00}{2} = 6{\cdot}50$$

$$y = \frac{b-s}{4} = \frac{17{\cdot}37 - 13{\cdot}00}{4} = \frac{4{\cdot}37}{4} = 1{\cdot}09.$$

Composition of slag—

$$6{\cdot}50(RO)_2 \,.\, SiO_2 + 1{\cdot}09RO \,.\, Al_2O_3.$$

Now spinel consists of RO (containing 1 of oxygen) and Al_2O_3 (with 3 atoms of O); hence the above calculated 1·09 molecule of spinel should contain $3 \times 1{\cdot}09 = 3{\cdot}27$ per cent. Al_2O_3, whereas only 2·30 per cent. Al_2O_3 is actually present. The slag can therefore only contain $\frac{2{\cdot}30}{3} = 0{\cdot}77$ spinel, whilst the rest of the basic oxygen, *i.e.* $17{\cdot}37 - 13{\cdot}00 - 4 \times 0{\cdot}77 = 17{\cdot}37 - 16{\cdot}08 = 1{\cdot}29$, must be present as free RO-bases. This gives the corrected composition of the slag as—

$$6{\cdot}50(RO)_2 \,.\, SiO_2 + 0{\cdot}77RO \,.\, Al_2O_3 + 1{\cdot}29RO.$$

It is thus evident that the spinel content in slag can be calculated, approximately at least, when the oxygen ratio is smaller than corresponds to singulo-silicate. On the other hand, in acid slags the spinel must be determined by direct analysis.

It must, however, be expressly mentioned that the calculation gives not only $RO \,.\, Al_2O_3$, but also $RO \,.\, Fe_2O_3$ and $RO \,.\, Mn_2O_3$.

With regard to the spinel content of a series of slags, the following tables, from the previously mentioned publications of J. H. L. Vogt, are now given, in order to afford a means

of comparison between the calculated and the actually determined values for this mineral:—

BLAST FURNACE SLAG ANALYSES BY MUIRHEAD.[1]

Constituents.	No. 128.	No. 129.	No. 130.	No. 131.	No. 132.	No. 133.
Percentage Composition,						
SiO_2	24·92	28·74	27·01	26·46	27·53	27·64
,, ,, Al_2O_3	23·47	25·63	20·13	23·44	22·23	22·93
,, ,, CaO	37·32	29·40	40·93	35·50	36·30	37·06
,, ,, MgO	13·23	13·75	11·09	13·34	13·00	12·95
Total . .	98·94	97·52	99·16	98·74	99·06	100·58
Spinel	17·40	17·88	10·82	8·18	6·07	9·04
Oxygen in SiO_2 . .	13·12	15·16	14·41	14·11	14·69	14·75
,, ,, Al_2O_3 . .	10·94	11·94	9·38	10·92	10·37	10·69
,, ,, CaO . .	10·66	8·40	11·69	10·16	10·37	10·59
,, ,, MgO . .	5·29	5·50	4·44	5·34	5·20	5·58
$\frac{\text{Acid oxygen}}{\text{Basic oxygen}}$ = . .	0·49	0·59	0·56	0·54	0·57	0·56
$\frac{\text{MgO oxygen}}{\text{CaO oxygen}}$ = . .	0·49	0·65	0·37	0·52	0·50	0·49

These slags can therefore contain only gehlenite and spinel.

COMPOSITION OF THE SLAG CONSTITUENTS SOLUBLE IN HCl AND HF.

In 100 Parts of Slag.	No. 128.	No. 129.	No. 130.	No. 131.	No. 132.	No. 133.
SiO_2	24·92	28·74	27·01	26·46	27·53	27·64
Al_2O_3	11·62	13·46	13·00	17·80	18·06	16·24
CaO	35·84	27·72	39·30	35·50	36·30	37·06
MgO	9·16	9·70	9·00	10·80	11·10	10·60
Total . .	81·54	79·62	88·31	90·56	92·99	91·54
Aluminate . . .	17·40	17·88	10·82	8·18	6·07	9·04
Total . .	98·94	97·50	99·13	98·74	99·06	100·58

[1] *Iron*, 15th Oct. 1880.

COMPOSITION OF THE ALUMINATES.

Constituents.	No. 128.	No. 129.	No. 130.	No. 131.	No. 132.	No. 133.
In 100 parts of slag: Al_2O_3	11·85	12·17	7·13	5·64	4·17	6·69
,, ,, CaO .	1·48	1·68	1·63	...	...	...
,, ,, MgO.	4·07	4·05	2·09	2·54	1·90	2·35
Total . .	17·40	17·90[1]	10·85[1]	8·18	6·07	9·04
Per 100 parts aluminate, Al_2O_3	68·11	69·98	65·88	68·92	68·72	74·00
,, ,, CaO	8·48	9·39	14·96	...	...	...
,, ,, MgO	23·41	22·63	19·16	31·08	31·28	26·00
Total . .	100·00	100·00	100·00	100·00	100·00	100·00
Oxygen in Al_2O_3 . .	5·57	5·72	3·35	2·65	1·96	3·14
,, ,, CaO . .	0·42	0·48	0·47	...	...	...
,, ,, MgO . .	1·63	1·62	0·84	1·02	0·76	0·94
Oxygen in RO-bases .	2·05	2·10	1·31	1·02	0·76	0·94
$\frac{Al_2O_3\text{-oxygen}}{RO\text{-oxygen}} =$ . .	2·71	2·72	2·56	2·59	2·58	3·34

Since spinel has the oxygen ratio 3 : 1, it is clear that the aluminates are not pure.

COMPOSITION OF SLAGS CALCULATED FROM FORMULÆ ALREADY GIVEN.

Substance.	No. 128.	No. 129.	No. 130.	No. 131.	No. 132.	No. 133.
Gehlenite . . .	6·56	7·58	7·21	7·06	7·35	7·38
Spinel	1·83	0·80	1·00	1·31	1·00	1·11
O in Spinel Al_2O_3 . .	5·49	2·42	3·00	3·96	3·02	3·33
,, RO . .	1·83	0·80	1·00	1·32	1·00	1·11

[1] Does not exactly agree with the value found direct.

On comparing these figures with those obtained direct, we find—

(*a*) All the aluminates containing CaO give throughout, in calculation, a smaller content of Al_2O_3RO.

(*b*) The aluminates free from CaO give throughout, in calculation, a larger proportion of Al_2O_3 and RO than by direct estimation.

The latter peculiarity can be explained by a partial decomposition of the MgO-aluminate, whilst the former could only be explained by the presence of inclusions in the spinel.

For the approximate calculation of the spinel, J. H. L. Vogt proposed the empirical formula [1]—

$$\text{Spinel} = C(1-a)\beta(\beta-4)\gamma(\gamma-8).$$

Here a indicates the oxygen ratio $\frac{s}{b}$ (wherein Al_2O_3 is reckoned as base), β and γ the percentages of MgO and Al_2O_3; C is a constant, and about $=\frac{1}{1200}$. Nevertheless, as Vogt himself admitted, this gives somewhat unreliable results.

Cal.	Found.	Cal.	Found.
about 20	17·68	about 13	6·07
„ 17	17·40	„ 3	about 6·5
„ 7	10·82	„ 4·5	„ 3
„ 13	9·04	„ 2	„ 2
„ 13	8·18	„ ½	„ ½

The accompanying table shows at a glance the equations employed for the calculation of the slags.

All that now remains is to fix the line of demarcation between the minerals belonging to one and the same stage of silication, which may be a matter of importance for many metallurgical operations. In order to obtain as good an

[1] For the basis of this see *Bihang till k. svenska Vet. Akad. Handlingar*, vol. ix. No. 1, p. 161.

b	Oxygen Ratio in the Mineral.	3:1.	2:1.	1:1.	2:3.	...
	Corresponding mineral	Globulites in acid enamel slags	Hexagonal lime silicate, $CaSiO_3$ Wollastonite, $CaSiO_3$ Augite, $Ca(Mg)SiO_3$ Rhodonite, $MnSiO_3$ Babingtonite, $n(MnR)SiO_3 + Fe_2Si_3O_9$ Enstatite, $MgSiO_3$ Hypersthene / Bronzite $(FeMg)SiO_3$	Olivine, Mg_2SiO_4 Fayalite, Fe_2SiO_4 Tephroite, Mn_2SiO_4 Monticellite, $Ca_2SiO_4 + Mg_2SiO_4$ Willemite, Zn_2SiO_4 Melilite $(RO)_{12}(Al_2O_3)_2(SiO_2)_9$ New tetragonal mineral, Akermanite $(R_4Si_3O_{10})$ [1]	Gehlenite $(RO)_3 Al_2O_3 . (SiO_2)_2$	Spinel, $RO . Al_2O_3$ Magnetite, $RO . Fe_2O_3$ Etc.
$>2{\cdot}0$	...	$\frac{s}{2} - b$	$3b - s$	..	...	...
$2{\cdot}0$ to $1{\cdot}0$	...	...	$s - b$	$b - \frac{s}{2}$	...	...
$1{\cdot}0$ to $0{\cdot}7$	$CaO \geqq 0{\cdot}7$ $(MgO + MnO + FeO)$	...	...	$\frac{3}{2}s - b$	$b - s$	...
$<0{\cdot}67$	do.	...	...	...	$\frac{s}{2}$	$\frac{1}{4}(b - \frac{s}{0{\cdot}67})$
$<1{\cdot}0$	$CaO < 0{\cdot}7$ $(MgO + MnO + FeO)$	...	...	$\frac{s}{2}$	...	$\frac{1}{4}(b - s)$

[1] Oxygen ratio $= \frac{6}{4} = 1{\cdot}50$. This mineral, which in point of silication corresponds to the mean between di-silicate and singulo-silicate, seems to act the part of a eutectic mixture. This is disregarded in calculating the composition of the slag.

[2] With reference to any eventual excess of RO-bases, see the former examples.

insight into the matter as possible, we will arrange them, according to Vogt, in the subjoined table:—

		Wollastonite.	Hexagonal CaO-Silicate.	Augite.	Rhodonite.	Enstatite (Hypersthene).
Di-Silicates	$\frac{MgO+MnO+FeO}{CaO}$	$<0{\cdot}25$		$0{\cdot}50$ to $1{\cdot}40$		$>2{\cdot}40$
	$\frac{CaO+MgO+FeO}{MnO}$	...	...	>3 to 4	$<0{\cdot}9$ to $1{\cdot}0$	...
	CaO	Predominating.		...	...	Little.
	MgO	Little.		...	...	Predominating.
	FeO	...	...	...	Little.	
	MnO	...	...	...	Predominating.	...

		New Tetragonal Non-aluminous Mineral: Akermanite.	Melilite.	Gehlenite.	Olivine.
Singulo- and basic Silicates	$\frac{CaO}{RO} = Al_2O_3$	$>1{\cdot}10$ to $1{\cdot}20:1$ 3 to 5 per cent.			$<1{\cdot}10$ to $1{\cdot}20:1$
	$\frac{CaO}{RO} Al_2O_3$	$>1{\cdot}1:1$ High.			$<1{\cdot}1:1$
	$\frac{CaO}{RO} Al_2O_3$	Still a little higher. Below 3 per cent.			Somewhat lower.
	s	1·30 to 1·50	1·30 to 0·80	$<0{\cdot}80$	$<1{\cdot}5$
	b				

At and between the limits of two adjacent minerals both may appear together.

G. Hilgenstock (*loc. cit.*) assumes that only the silicate RO. SiO_2 is present in slags. He says on this point:—

"With regard to our blast-furnace slags, as we desire to obtain them from the large parcels of material at our disposal,

we generally calculate according to the formula $(RO)_2 . SiO_2$, and measure out the addition of lime accordingly, knowing, as we do, that a silicate slag, in which the total oxygen of the bases is equal to the oxygen of the silica, will possess a suitable fusibility, *i.e.* is sufficiently fluid at a given temperature; and we do not trouble about the fact that such slags already contain considerable quantities of 'free lime,' merely 'dissolved.' Should, however, it appear that the solvent capacity of the slag for free lime is being overtaxed in consequence of an alteration in the material,—the furnace temperature and the composition of the slag being otherwise unchanged,—which condition is manifested by the quick solidification and disintegration of the refractory slag, then, if the lime evil seems inconvenient, we reduce the quantity of lime (and therefore the amount of 'free lime' in the slag) as quickly as possible, though we may find later that the proportion of RO in the refractory slag was lower than in that which was sufficiently fusible at the same temperature. In the solvent capacity for free lime alone have I been able to find an explanation of the behaviour of blast-furnace slag in a number of observations.

"Consequently the content of free lime teaches that there can be no question of the presence of a compound R_2SiO_4 in our (lime-) basic blast-furnace slags, although their constitution works out approximately to $(RO)_2 . SiO_2$.

"If from a blast-furnace slag of the following composition—

SiO_2	34·18 per cent.
FeO	1·14 ,,
MnO	3·93 ,,
CaO	39·26 ,,
Al_2O_3	16·73 ,,
MgO	2·32 ,,
CaS	4·23 ,,

we extract as much as possible of the free lime by means of a suitable sugar solution, we obtain 37 CaO to 39 SiO_2, from whence it follows that the quantities are fairly equivalent, that the silicate of our slags is calcium silicate $CaO . SiO_2$, and that it belongs to the carbon dioxide type, corresponding to the acid H_2SiO_3."

This opinion of Hilgenstock's contradicts the finding of the microscope, and we must therefore examine whether his reasons are forced or not. In the first place, the existence of both the meta- as well as of the orthosilicic acid has been proved, inasmuch as not only a number of silicates corresponding thereto, but also the free acids themselves, are known; it therefore seems possible for slags to contain orthosilicates.

Moreover, the conclusion that the silica in slag can only be in combination with lime, seems very hazardous, since numerous decided double silicates are known, and therefore the possibility of the formation of other silicates cannot be disputed. It may be admitted at once that the affinity of silica for CaO is greater than for FeO, MnO, Al_2O_3, etc.; but, in accordance with the law of mass, it is certain that in presence of all these bases the silica will not restrict itself exclusively to lime, but must also combine with the others, to an extent determined by its affinity therefor on the one hand, and their relative proportion on the other. Consequently the other bases cannot by any means be neglected.

On calculating the oxygen ratio of the above slag, we have—

	Per cent.		Per cent.	
SiO_2	34·18	containing oxygen	**18·21** = *a*	
FeO	1·14	„ „	0·25	
MnO	3·93	„ „	0·87	
CaO	39·26	„ „	11·22	**21·14** = *b*
Al_2O_3	16·73	„ „	7·87	
MgO	2·32	„ „	0·93	
CaS	4·23			

$$\frac{\text{Acid oxygen}}{\text{Basic oxygen}} = 0{\cdot}86.$$

According to Hilgenstock, the slag must contain a silicate of the composition—

SiO_2 .	34·18	per cent.	containing oxygen	18·21	per cent.
CaO .	31·61	„	„	9·11	„
	65·79	per cent.			

wherein are dissolved—

	Per cent.		Per cent.	
Free CaO . .	7·65	containing oxygen	2·11	
FeO . . .	1·14	„ „	0·25	
MnO . . .	3·93	„ „	0·87	12·03
MgO . . .	2·32	„ „	0·93	
Al_2O_3 . . .	16·73	„ „	7·87	
CaS . . .	4·23			

whereas, according to the formulæ already given, the composition of the slag would work out to—

$$8{\cdot}17\ (RO)_2 . SiO_2 + 2{\cdot}92\ (RO)_3 . SiO_2$$

(leaving the formation of sesquioxide compounds out of the question altogether).

According to Hilgenstock, the residue insoluble in the sugar solution contains—

39 SiO_2,	of which	19·61 = oxygen
37 CaO	„	10·57 „

whence he concludes that the same is a bi-silicate (which should contain, to 19·61 acid oxygen, 9·80 basic oxygen). Now in Hilgenstock's reports there is a deficiency of 24 per cent. If we assumed the 39 per cent. SiO_2 of the residue to exactly represent the 34·18 per cent. in the slag, and that all the other constituents (except the lime dissolved by the sugar) remained in the residue, then its composition would be—

Per cent.			Per cent.	
39·00	SiO_2 containing	oxygen	**19·61**	
37·00	CaO	,, ,,	10·57	
1·30	FeO	,, ,,	0·37	
4·48	MnO	,, ,,	1·28	**22·25**
19·09	Al_2O_3	,, ,,	8·98	
2·64	MgO	,, ,,	1·05	
4·84	CaS			
108·35				

As, however, the total would come to 108·35 per cent., there must be something more than CaO passed away in the solution; and even after deducting the 4·89 per cent. of CaS, which would certainly be decomposed and dissolved, there still remain 103·51 per cent. Further, assuming—as would be not improbable in view of the oxygen ratio and the high alumina content of this slag—that magnesia is present in the form of aluminate, that this is decomposed by the sugar solution, and that the MgO is also dissolved, then the total would be = 100·87, and we should obtain, to 19·61 acid oxygen, 21·20 basic oxygen. Moreover, if we remember that the latter still contains $3 \times 1{\cdot}05 = 3{\cdot}15$ oxygen from the alumina of the decomposed aluminate, we shall obtain the ratio—

$$\frac{\text{Acid oxygen}}{\text{Basic oxygen}} = \frac{19{\cdot}61}{21{\cdot}20 - 3{\cdot}15} = \frac{19{\cdot}61}{18{\cdot}05} = 1{\cdot}08,$$

which comes very near to the oxygen ratio 1 : 1, corresponding to the silicate $(RO)_2 . SiO_2$.

The behaviour of the slag observed by Hilgenstock can therefore be very well explained by either regarding the compound $(RO)_3 . SiO_2$ as a solution of RO in $(RO)_2 . SiO_2$, or by assuming that the compound $(RO)_3 . SiO_2$ is decomposed into $(RO)_2 . SiO_2 + RO$ by the sugar solution.

CHAPTER IV

PHOSPHATE SLAGS

In this case, also, we will first devote attention to the various known hydrates. These are—

di-basic or metaphosphoric acid—

$$H_2PO_5 \text{ or } \begin{matrix} O \\ O \end{matrix}\!\!\gg\!P-O-H$$

tri-basic or orthophosphoric acid—

$$H_3PO_4 \text{ or } O=P\begin{matrix} O-H \\ O-H \\ O-H \end{matrix}$$

tetra-basic pyrophosphoric acid—

$$H_4P_2O_7 \text{ or } \begin{matrix} H-O \\ H-O \end{matrix}\!\!\rangle P-O-P\langle\!\!\begin{matrix} O-H \\ O-H \end{matrix}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad \| \qquad\quad \|$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad O \qquad\quad O$$

or—

$$\begin{matrix} H-O \\ H-O \end{matrix}\!\!\rangle P\begin{matrix} \diagup O \diagdown \\ -O- \\ \diagdown O \diagup \end{matrix}P\langle\!\!\begin{matrix} O-H \\ O-H \end{matrix}$$

octa-basic pyrophosphoric acid—

$H_8P_2O_9$[1] or

$$\begin{matrix} H-O \\ H-O \\ H-O \\ H-O \end{matrix}\!\!\rangle P-O-P\langle\!\!\begin{matrix} O-H \\ O-H \\ O-H \\ O-H \end{matrix}$$

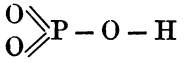
[1] Kosmann assumes the constitution of the calcium phosphate to be—

$$Ca<\begin{matrix} O \\ O \end{matrix}>PO-O-Ca-O-Ca-O-PO<\begin{matrix} O \\ O \end{matrix}>Ca.$$

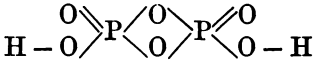
The only representatives known of this last acid are the tetra-calcium phosphate found in Thomas slag, and "Wiborgh phosphate," $Ca_3Na_2P_2O_9$.

The following polymeric modifications originate from metaphosphoric acid:—

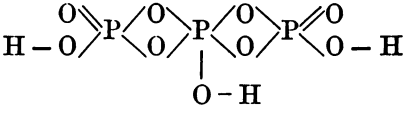
Metaphosphoric acid—



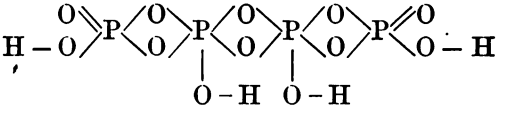
di-metaphosphoric acid—



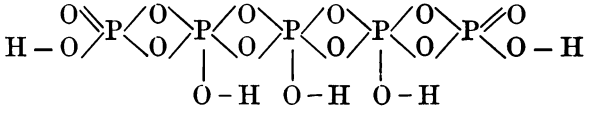
tri-metaphosphoric acid—



tetra-metaphosphoric acid—

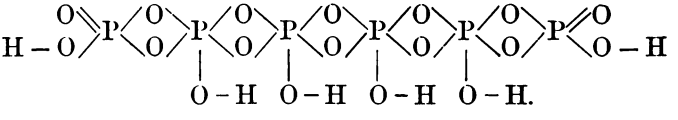


penta-metaphosphoric acid—



(which has not yet been isolated), and

hexa-metaphosphoric acid—



Hilgenstock[1] was the first to prove the appearance of phosphoric acid in the form of tetra-basic (or, more correctly, octa-basic) calcium phosphate ($4CaO \cdot P_2O_5 = Ca_4P_2O_9$) in Thomas slag.

[1] *Stahl u. Eisen*, 1886, ii.

Stead and Ridsdale[1] found the Thomas slag of the North Eastern Steel Company to contain—

1. Large well-developed crystals of $(CaO)_4 . P_2O_5$.
2. Blue crystals of the compound $CaOP_2O_5 . CaOSiO_2$.
3. Feathery crystals containing over 86 per cent. of basic oxides, chiefly Ca, Mg, Fe (as ferrous and ferric oxides), and Mn, together with less than 4 per cent. of acid oxides.
4. Hexagonal crystals containing about 86 per cent. $(CaO)_4 . P_2O_5$ and 10–11 per cent. of metallic-oxide silicates.
5. Black magnetic needles consisting of 10 per cent. $CaO . Al_2O_3$, 45 per cent. $(CaO)_3 . Fe_3O_4$, and 33·5 per cent. $(CaO)_3Fe_2O_3$.
6. Black non-magnetic crystals, of 15 per cent. $CaO . Al_2O_3$ and 73 per cent. $(CaO)_3 . Fe_2O_3$.

By fusing together tri-calcium phosphate (or di-calcium phosphate and phosphoric anhydride) with a corresponding amount of quicklime and a little fluorspar, Hilgenstock[2] afterwards succeeded in obtaining the pure compound in crystalline needles, corresponding to the hexagonal prisms in Thomas slag. Their average composition was—

P_2O_5	38·51 per cent.
CaO	60·08 ,,
SiO_2	0·10 ,,

The crystals were always colourless and clear, and contained fewer inclusions than those from Thomas slag, which latter are invariably brown or clouded from the presence of metallic oxides.

Whilst the phosphate in Thomas slag does appear as hexagonal prisms, it is chiefly in rhombic plates, as well as in

[1] *Journ. Iron and Steel Inst.*, 1897, vol. i.
[2] *Stahl u. Eisen*, 1887, p. 557.

small brilliant blue crystals, of diamond lustre, belonging (according to Bücking and Linck[1]) to the monoclinic system.

The serial order in which these are deposited is—

1. Rhombic plates (deposited at the highest temperature).
2. Hexagonal prisms (needles) (separating out at lower temperatures from the solution already impoverished of phosphates).
3. Blue, lustrous monoclinic crystals (deposited still later).

The latter crystals are accompanied by fern-like tufts of black crystals, which Stead and Ridsdale[2] report to consist of calcium ferrate and aluminate.

This also explains why it is that no rhombic plates were obtained in crucible smelting tests—since here the temperature is far below that in the converter.

The crystals of tetra- (or octa-) basic calcium phosphate invariably contain large inclusions of foreign substances, as is shown by the following analyses:—

A. Hexagonal Prisms.

Constituent.	G. Hilgenstock.	Stead.	Bücking and Linck.
	Per cent.	Per cent.	Per cent.
P_2O_5	34·94	33·707	36·77
CaO	57·55	53·536	53·51
MgO	...	0·486	0·40
Fe_2O_3	...	4·857	1·78
FeO	4·00	1·286	2·22
MnO	...	0·790	...
VO	...	1·343	...
SiO_2	3·24	3·900	3·81
S	...	0·460	trace
Cl	...	...	trace
Al_2O_3	...	...	1·09

[1] *Stahl u. Eisen*, 1887, p. 245.

[2] *Loc. cit.*

B. Rhombic Plates.

Bücking and Linck.

P_2O_5	38·77 per cent.
CaO	59·53 „
MgO	trace
$Fe_2O_3 + Al_2O_3$	0·89 „
MnO	strong trace
SiO_2	0·89 per cent.
S	0·28 „
	100·36

C. Blue Monoclinic Crystals.

Constituent.	G. Hilgenstock.	Stead.	Bücking and Linck.
	Per cent.	Per cent.	Per cent.
P_2O_5	30·85	29·146	31·19
CaO	57·60	56·578	57·42
MgO	...	0·738	trace
Fe_2O_3	...	1·000	...
Al_2O_3	...	trace	1·13
FeO	2·94	...	0·95
MnO	...	0·210	trace
SiO_2	9·42	10·791	9·47
S	...	0·055	trace

All these results correspond to the formula $Ca_4P_2O_9$, and show that the crystals contain inclusions of somewhat variable composition.

Mention should here be made of the so-called "retrogradation" of phosphoric acid, *i.e.* the change of the phosphates, soluble in citric acid, into an insoluble form. O. Förster[1] found that $Ca_4P_2O_9$, when heated for a short time to a point a few hundred degrees below its temperature of formation, suffered a change, inasmuch as a large part of the phosphoric acid previously soluble in citric acid became insoluble. The insoluble residues proved to be $(Ca_3P_2O_8)_3 . CaO$ and (in presence of sufficient silica) $(Ca_3P_2O_8)_3 . CaSiO_3$.

[1] *Zeits. f. angew. Chem.*, 1892, p. 13.

Whilst this conversion is of a very extensive character in the case of pure calcium tetraphosphate, it is limited to a comparatively small portion of the phosphate in the case of Thomas slag. Heating to redness in hydrogen produces the same effect as in air, but to a smaller extent. In the latter case probably the carbon dioxide formed in the blast flame, and the oxidising action of atmospheric oxygen on other constituents of the slag, have all to be reckoned with; and probably $CaO.FeO$ or $CaO.Fe_2O_3$ is formed at the same time. FeS and $MnO.Fe_2O_3$ may also take part in the reaction ($2CaO + 2FeS + 3O = 2CaS + Fe_2O_3$; or $2CaO + MnO.Fe_2O_3 + O = CaO.Fe_2O_3 + CaO.MnO_2$). Moreover, not only does the lime separated from the $Ca_4P_2O_9$ enter into insoluble combinations, but the same is done by the pre-existing free lime present.

The remaining constituents of Thomas slag will be dealt with under the oxide slags. Meanwhile it will be sufficient to point out that the calculation of the composition of this slag is performed by first reckoning up the calcium tetraphosphate from the phosphoric acid found, the remainder being then calculated as silicate or oxide slag.

Examples.

(*a*) *Basic Martin Furnace Slag.*

	Per cent.		Per cent.
SiO_2 . . .	13·90	containing oxygen	**7·41** = *s*
P_2O_5 . . .	2·30	„ „	1·30
Al_2O_3 . . .	2·80	„ „	1·31
FeO . . .	24·62	„ „	5·47
MnO . . .	10·41	„ „	2·34
CaO . . .	39·50	„ „	11·27
MgO . . .	5·76	„ „	2·30

The 1·30 O of the P_2O_5 corresponds to $1{\cdot}30 \times 0{\cdot}80 = 1{\cdot}04$ oxygen in lime (which together give $\frac{1{\cdot}04}{4} = 0{\cdot}26$ mol. $Ca_4P_2O_9$).

Hence, after deducting the oxygen in the calcium phosphate, we have—

		Per cent.	
Oxygen in	SiO_2	7·41	$= s$
,,	Al_2O_3	1·31	
,,	FeO	5·47	
,,	MnO	2·34	$= 21·65 = b$
,,	CaO	10·23	
,,	MgO	2·30	

$$\frac{s}{b} = 0·34$$

$$\frac{MgO + MnO + FeO}{CaO} = 0·99.$$

On calculating the whole of the alumina to spinel, we find the composition of the slag—

0·26 mol. Calcium phosphate ($Ca_4P_2O_9$).
3·71 ,, Olivine (R_2SiO_4).
0·44 ,, Spinel.
12·48 ,, Free RO-bases.

(*b*) *Basic Martin Furnace Slag.*

	Per cent.			Per cent.
SiO_2	13·97	containing	oxygen	7·44
P_2O_5	1·83	,,	,,	1·03
Al_2O_3	5·17	,,	,,	2·43
FeO	20·61	,,	,,	4·58
MnO	12·12	,,	,,	2·73
CaO	40·26	,,	,,	11·50
MgO	6·44	,,	,,	2·58

The 1·03 oxygen in P_2O_5 corresponds to 0·82 of lime oxygen ($= 0·21$ $Ca_4P_2O_5$), thus leaving—

		Per cent.	
Oxygen in	SiO_2	7·44	$= s$
,,	Al_2O_3	2·43	
,,	FeO	4·58	
,,	MnO	2·73	$= 26·86 = b$
,,	CaO	10·68	
,,	MgO	6·44	

$$\frac{s}{b} = 0·27$$

$$\frac{MgO + MnO + FeO}{CaO} = 1·29.$$

Thus, taking the same view as before, this slag would consist of—

0·21 mol. Calcium phosphate.
3·72 „ Olivine.
0·81 „ Spinel.
16·18 „ Free RO-bases.

(*c*) *Basic Martin Slag low in Phosphorus.*

	Per cent.		Per cent.
SiO_2 . .	23·77	containing oxygen	12·66
P_2O_5 . .	0·379	„ „	0·213
Al_2O_3 . .	1·34	„ „	0·63
Fe_2O_3 . .	2·59	„ „	0·77
FeO . .	14·24	„ „	3·16
MnO . .	29·06	„ „	6·46
CaO . .	11·22	„ „	3·21
MgO . .	16·90	„ „	6·76
S . . .	0·175 (assumed to be combined with Ca).		

To this 0·213 P_2O_5 = oxygen corresponds 0·16 lime oxygen, and there therefore remains—

	Per cent.	
Oxygen in SiO_2 . . .	**12·66** = *s*	
„ Al_2O_3 . . .	0·63	
„ Fe_2O_3 . . .	0·77	
„ FeO . . .	3·16	**20·83** = *b*
„ MnO . . .	6·46	
„ CaO . . .	3·05	
„ MgO . . .	6·76	

$$\frac{s}{b} = 0{\cdot}61$$

$$\frac{MgO + MnO + FeO}{CaO} = 5{\cdot}37.$$

The slag therefore consists of—

0·04 mol. Calcium phosphate.
6·33 „ Olivine.
0·47 „ Spinel and magnetite.
5·29 „ Free RO-bases.

(*d*) *Thomas Slag.*

	Per cent.			Per cent.	
SiO_2 .	11·71	containing	oxygen	6·24	
P_2O_5	18·15	,,	,,	10·23	
Al_2O_3	1·01	,,	,,	0·47	
Fe_2O_3	2·78	,,	,,	0·83	
FeO .	7·19	,,	,,	1·60	
MnO	4·05	,,	,,	0·91	0·91 − 0·05 = 0·86
CaO .	48·19	,,	,,	13·77	
MgO	6·38	,,	,,	2·50	
S .	0·09	corresponding to		0·05	

The 10·23 oxygen in the P_2O_5 correspond to 8·18 in CaO (2·05 $Ca_4P_2O_9$), and there then remains—

	Per cent.	
Oxygen in SiO_2 . . .	**6·24** = *s*	
,, Al_2O_3 . . .	0·47	
,, Fe_2O_3 . . .	0·83	
,, FeO . . .	1·60	**11·85** = *b*
,, MnO . . .	0·86	
,, CaO . . .	5·59	
,, MgO . . .	2·50	

$$\frac{s}{b} = 0{\cdot}53$$

$$\frac{MgO + MnO + FeO}{CaO} = 0{\cdot}89.$$

Hence, for the mineralogical composition of the slag we obtain—

2·05 mol. Calcium phosphate.
3·12 ,, Olivine.
0·43 ,, Spinel and magnetite.
3·87 ,, Free RO-bases.

N.B.—Strictly speaking, the calculation of spinel and magnetite from the total $Al_2O_3 + Fe_2O_3$ is not correct; but it can always be regarded as approximately so.

In lime-free refinery slags, *e.g.* puddling slag, the conditions are somewhat different, the bulk of the phosphoric acid

being necessarily combined with other bases in the absence of a sufficiency of lime to take the whole. In this connection MnO appears to play a leading part, the analyses of three puddling slags prepared from the same raw materials, in different furnaces, giving the following results:—

	I. %	II. %	III. %
SiO_2 . . .	16·75	14·08	14·89
Fe_2O_3 . . .	16·00	28·61	17·79
FeO . . .	33·84	30·93	50·36
MnO . . .	26·29	20·59	13·18
CaO . . .	1·34	1·27	0·92
MgO . . .	0·57	0·49	0·49
P_2O_5 . . .	4·65	3·60	1·90
MnS . . .	0·76	0·52	0·57

The calculation of the ratio $\frac{MnO}{P_2O_5}$ gives—

	5·56	5·69	6·90,

the phosphoric acid content being therefore nearly proportional to the percentage of manganese.

This becomes still clearer when CaO is taken into consideration as well as MnO, the values for the oxygen being then—

	I.		II.		III.	
In MnO .	5·93	6·31	4·64	5·0	2·97	3·23
„ CaO .	0·38		0·36		0·26	
„ P_2O_5 .	2·62		2·03		1·07	

and the oxygen ratio in—

$\frac{MnO+CaO}{P_2O_5}$ =	2·41	2·46	3·01

Should the MnO be insufficient to combine the whole of the P_2O_5, then FeO would probably come into action.

Though it has been determined with certainty that the only calcium phosphate appearing in phosphate slags is $Ca_4P_2O_9$, opinions differ regarding the FeO and MnO phos-

phates; some believe them to be tri-basic,[1] and therefore corresponding to $Mn_3P_2O_8$ and $Fe_3P_2O_8$, whilst others also speak in favour of tetrabasic[2] phosphates ($Mn_4P_2O_9$ and $Fe_4P_2O_9$). Fortunately, this does not make much difference to the results of the slag calculations, the amount of basic oxygen corresponding to the P_2O_5-oxygen being found in the first case by multiplying with the factor 0·6, and in the second case by using 0·8. The number of molecules of phosphate remains the same, only in the former case the amount left over for the silicates is a little greater.

This will be clearer from the following example, taken from the first of the above puddling slag analyses :—

Oxygen in	SiO_2 . . .	8·92 per cent.
,,	Fe_2O_3 . .	4·80 ,,
,,	FeO . . .	7·52 ,,
,,	MnO . .	5·93 ,,
,,	CaO . . .	0·38 ,,
,,	MgO . .	0·23 ,,
,,	P_2O_5 . . .	2·62 ,,

The 0·38 lime oxygen corresponds to 0·48 P_2O_5-oxygen; thus leaving $2·62 - 0·48 = 2·14$ P_2O_5-oxygen for the RO-bases.

If we assume in the first place that octabasic phosphates are formed here, then the 2·14 P_2O_5-oxygen corresponds with 1·71 RO-oxygen, and there remains—

		Per cent.	
Oxygen in	SiO_2 . . .	**8·92** = s	
,,	Fe_2O_3 . . .	4·80	**16·77** = b
,,	FeO . . .	7·52	
,,	MnO . . .	4·22	
,,	MgO . . .	0·23	

$$\frac{s}{b} = 0·53.$$

[1] Or really hexabasic.

[2] More properly octabasic.

From this we obtain by calculation the following as tl mineralogical composition of the slag:—

0·10 mol. Calcium phosphate ($Ca_4P_2O_9$).
0·43 „ Manganese phosphate ($Mn_4P_2O_9$).
4·46 „ Olivine.
1·60 „ Magnetite.
1·45 „ Free RO-bases.

If, on the other hand, we assume the existence of hexabasic manganese phosphate, then the 2·14 P_2O_5-oxyg corresponds with 1·28 RO-oxygen, leaving—

		Per cent.	
Oxygen in	SiO_2 . . .	**8·92** = s	
„	Fe_2O_3 . . .	4·80	
„	FeO . . .	7·52	**17·20** = b
„	MnO . . .	4·65	
„	MgO . . .	0·23	

$$\frac{s}{b} = 0{\cdot}52$$

giving the slag the composition—

0·10 mol. Calcium phosphate ($Ca_4P_2O_9$).
0·43 „ Manganese phosphate ($Mn_3P_2O_8$).
4·46 „ Olivine.
1·60 „ Magnetite.
1·88 „ Free RO-bases.

CHAPTER V

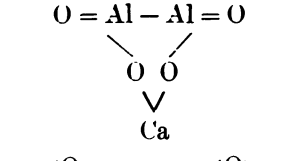
OXIDE SLAGS

VERY little is known as to the detailed composition of the oxide slags. Certain it is that the sesquioxide bases enter into combination with the monoxide bases; but whereas most observers have chosen for these compounds the formula $RO . R_2O_3$, Stead and Ridsdale[1] assume the existence of the compounds $CaO . Al_2O_3$; $(CaO)_3 . Fe_2O_3$ and $(CaO)_3Fe_2O_4$. As already mentioned, they found in Thomas slag two structural elements of the following composition:—

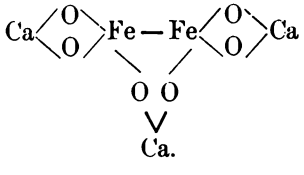
(*a*) Black magnetic needles, 10 per cent. $CaO . Al_2O_3$ + 45 per cent. $(CaO)_3Fe_3O_4$ + 33·5 $(CaO)_3 . Fe_2O_3$.

(*b*) Black non-magnetic crystals, 15 per cent. $CaO . Al_2O_3$ + 73 per cent. $(CaO)_3 . Fe_2O_3$.

The theoretical possibility of the compounds $RO . R_2O_3$ and $(RO)_3 . R_2O_3$ cannot be disputed, since they may be represented by the following constitutional formulæ:—

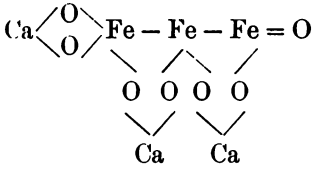


and—



[1] *Stahl u. Eisen*, 1887, p. 557.

Finally, the constitutional formula—



can be laid down for the presumptive compound $(CaO)_3 . Fe_3O_4$. It is therefore quite possible that—as in the case of spinel, etc.—only the compound $RO . R_2O_3$ really exists, but is able to crystallise with excess of RO and R_2O_3, this latter assumption being supported by the parallel cases of natural magnetic ironstone, etc., wherein both monoxide bases and sesquioxide bases are found in excess.

To decide these questions necessitates thorough investigation, especially of the fusion curves of this class of slags. In the meantime it suffices for practical purposes to regard these slags as mixtures (or solutions) of $RO . R_2O_3$ and RO (or R_2O_3).

Of course the slags may also contain small quantities of phosphates, sulphides, and fluorides.

A special class of oxide slags occurs under certain circumstances in the form of inclusions in iron alloys. A characteristic feature of these bodies is their poverty in sesquioxides (apart from the accidental presence of alumina), the cause of this being that these oxides are at once reduced to the state of monoxides by the adjacent excess of metal.

These inclusions consist of a mixture of monoxides with silicates and fluorides, though, under certain circumstances, the silicates are very much in the background. Of course phosphates may also be present.

Examples of the composition of such inclusions are contained in the following tables:—

Constituents.	I.	II.	III.	IV.	V.
	%	%	%	%	%
SiO_2	6·01	8·33	10·0	21·44	27·81
P_2O_5	...	...	...	0·54	0·84
Al_2O_3	0·49	...	trace	0·83	0·28
FeO	29·27	...	22·60	24·25	17·19
MnO	59·65	59·61	67·36	24·73	24·71
CaO	0·91	...	...	17·24	14·41
MgO	0·33	...	...	9·58	19·21
Mn	2·16	...	3·10	1·02	0·24
S	1·26	...			0·14
Total	100·08	...	103·56	99·63	104·83

N.B.—The considerable divergence from 100 in several of the analyses is due to the extreme smallness of the samples available for examination.

The oxygen content of the above slags is given below :—

Oxygen in—	I.	II.	III.	IV.	V.
	%	%	%	%	%
SiO_2	3·20	4·44	5·33	11·42	14·81
P_2O_5	...	...	...	0·30	0·47
Al_2O_3	0·21	...	trace	0·39	0·13
FeO	6·50	...	5·02	5·39	3·82
MnO	13·44	13·43	15·18	5·57	5·56
CaO	0·26	...	...	4·93	4·12
MgO	0·13	...	...	3·83	7·68
CaO in phosphate	...	...	...	0·24	0·38
Equivalent to the S	0·63	...	0·56	0·19	0·07
Available basic oxygen	20·54	...	20·20	19·87	20·93
Oxygen ratio of the silicate	0·15	...	0·26	0·57	0·71

From which the composition of the slag works out to—

Mol.	I.	II.	III.	IV.	V.
	%	%	%	%	%
Olivine	3·20	4·44	5·33	11·42	14·81
Calcium phosphate . .	...	?	...	0·06	0·10
Manganese sulphide . .	0·63	?	0·56	0·19	0·07
Free RO-bases . . .	17·34	?	14·97	8·45	6·12

The following slag from Soaking Pits is not devoid of a certain interest:—

	Per cent.		Per cent.
SiO_2 . .	3·14	containing oxygen . .	1·67
P_2O_5 . .	0·068	„ „ . .	0·039
Fe_3O_4 . .	24·77	„ „ . .	6·83
FeO . .	68·31	„ „ . .	15·18
MnO . .	1·047	„ „ . .	0·232
CaO . .	1·03	„ „ . .	0·294
MgO . .	0·83	„ „ . .	0·332
S . .	0·021	corresponding to oxygen	0·0105

$$\text{Stage of silication} = \frac{1·67}{22·73} = 0·07.$$

From this the composition of the slag works out as follows:—

	Per cent.
Manganese sulphide	0·011
Calcium phosphate	0·008
Gehlenite $(RO)_3 (SiO_2)_2$	0·84
Magnetite	1·71
Free RO-bases	13·48

In conclusion, reference should be made to the relation existing between slags and fireproof materials. The former are comparatively readily fusible mutual solutions of several very refractory bodies; consequently fireproof materials may be regarded as the more refractory members of the slag series. This purely theoretical aspect of the aforesaid relation has, however, its practical side, since it leads to the rule that, in selecting fireproof materials for building furnaces, choice should fall on such as are the least, if at all, soluble in the slags to be produced in the furnaces in question.

APPENDIX TO PAGES 226 AND 233

THE recently published researches of Bakhuis and Roozeboom [1] have led to a modification of previous opinion, inasmuch as, on the basis of Rothmund's formula,[2] they furnish another deduction for the molecular dimensions m of the dissolved carbon. The Rothmund formula runs—

$$t_0 - t_1 = \mathrm{E}\frac{c_1 - c_2}{m},$$

t_0 being the fusing point of iron, t_1 the lower temperature at which a melt with c_1 per cent. of C deposits solid crystals containing c_2 per cent. of C. The crystals here implied are those first formed, or, in other words, those which at $t_1°$ may be in equilibrium with the melt c_1.

E is the constant of depression, which is equal to $\frac{0{\cdot}02\ \mathrm{T}^2}{\mathrm{W}}$, wherein $\mathrm{T} = 273 + t_0$, and W is the heat of fusion in calories per unit of weight. In the deposition of pure iron, E is the depression through 1 mol. carbon dissolved in 100 grms. iron. All the published calculations suffer from the defect that the value of W is not exactly known. If, like other workers, we take it as = 20 calories, then $\mathrm{E} = 3273°$.

Now the curve A B (Fig. 58) appears to be straight from 1600° to 1250° C. If, then, the still undetermined curve (for the solid bodies depositing at the various temperatures) to 1250° is also straight, it follows that the carbon has

[1] *Zeits. f. phys. Chemie*, xxxiv. (4), p. 479.
[2] *Ibid.*, xxiv. p. 705.

the same molecular dimensions both in solid and liquid solution, and the value can be calculated thus:—

$$m = \mathrm{E}\frac{c_1 - c_2}{t_0 - t_1}.$$

For $t_1 = 1250°$, $c_1 = 2{\cdot}85$ per cent. (bend in the line AB), and if the position of the said unknown curve be' correct (see Roozeboom's treatise), $c_2 = 1{\cdot}50$ per cent. Hence—

$$m = 3273 \times \frac{2{\cdot}85 - 1{\cdot}50}{1600 - 1250} = 12{\cdot}62,$$

and the carbon in liquid solution is monatomic. If this be so, it follows that the carbon in the mixture of crystals separating out between 1600° and 1250° is also in the monatomic condition.

In this place the equation of Heycock and Neville (used on pp. 226 and 234) may be given in its proper form—

$$\mathrm{M} = \frac{0{\cdot}0198}{w} m \frac{(\mathrm{T} - t)^2}{t}$$

whence the values of M and n adjust themselves as follows:—

m.	M.	n.
1·01	21·450	1·788
1·52	21·059	1·755
1·83	21·264	1·772
2·46	20·086	1·674
2·88	19·296	1·608
3·52	18·903	1·575
4·49	18·617	1·551

Similarly, on p. 234 we obtain—

$$\mathrm{M} = 298{\cdot}90$$
$$n = 6{\cdot}63$$

and for the carbide the formula: 1·66 Fe_3C.

THE END.

INDEX

ABEL's researches on iron alloys, 158, 184.
Acetone, 40.
Acid Bessemer steel, 267.
—— carbazeic, 179.
—— mellithic, 153.
—— nitrographitoic, 179.
Acids, their effect on iron carbide, 168.
"Adsorption, phenomena of," 43.
Agglomerations, radial, 98.
Akermanite, 140.
Akerman's temperatures of formation and fusion of slags, 296.
Alcohol, 40.
Alkali metals, nitrates of, 63.
Allotropic forms of pure iron, 237.
Alloy, eutectic, 16.
—— fusing point of, 14.
—— of tin and gold, 35.
—— solubility of, 14.
Alloys, metallic, 2.
—— molten, 14.
—— of copper and antimony, 77 (Figs. 29 and 30).
—— of copper and lead, 97, 98.
—— of copper with aluminium, 77 (Figs. 29 and 30).
—— of copper and tin, 98.
—— of iron, 2, 7.
—— of iron, chemical composition of, 144.
—— of tin and bismuth, 42.
—— silver-copper, 14 (Plate I. Fig. 3).
—— specific heat of, 80.
—— volume of, 79.
—— and iron, 237.
Alumina, 138.
Alumina-lime-magnesia-singulo-silicates, 295.
Alumina-lime-singulo-silicates, 294.
Aluminates, composition of, 309.
Aluminium, 150, 151.
Amorphous carbon, 148, 154.
—— solid bodies, 57.
Analysis, fractional, 93.
Anatomico-histological metallography, 82.
Anethol, 40.
Anions, 70.
Annealed steel, 116.
Annealing, 91.
Antimony, 144.
—— dissolved in tin, 53.
Apparatus showing loss of carbon, 193.
Aqueous solution, 7.
Arnold's tensile errors exposed by Sauveur, 240 (Plate X. Fig. 84).
Arsenic, 144.
Augite, 137.
—— in slags, 299.
Aureoles in graphite scales, 125.
Austenite, 100 (Plate VIII. Fig. 55), 117, 121, 123, 130, 172, etc.
—— points determined by Ormond, 230.
Avogadro's law, 22, 38.
Azobenzol, 40.

BAKHUIS and Roozeboom on carbon, 333 (Fig. 58).
Basic Bessemer steel, 267.
—— Martin furnace slag, 322, 323.
—— Martin slag low in phosphorus, 324.
—— slags, 301.
Behrens' method of fractional analysis, 93.
Benzol, 40.
Bessemer ingot iron, 146.

Bessemer products, 278.
—— steel, 146.
—— steel, acid, 267.
—— steel, basic, 267.
Biological metallography, 82.
Bismuth, 144.
—— and tin, alloys of, 42.
Blast-furnace graphite, 152.
—— slag analysed by Muirhead, 388.
Blooming iron, 146.
Blue monoclinic crystals in phosphate slags, 320, 321.
Bofors, iron ore from, 214, 215.
Boyle's law, 21, 23.
Bronzes, 50–52 (Figs. 17–26).
Bubble cavities, gases in, 274.
Bubbles, gas, 100–103 (Plate IV. Figs. 35–37).
—— on crystal surfaces of scorched steel, 103 (Plate IV. Fig. 39).
—— origin of, 180.
Burnished steel, 146.
Burnt iron, 257.

CADMIUM-BORATE, for treating ferro-chrome, 272.
Calcareous olivine, 139.
Calcium chloride for etching, 89.
Calculation of slags, equations for, 310.
Calescence points, 131.
Campbell's researches on combined carbon, 216–222.
Carbazeic acid, 179.
Carbide and hardening carbon, author's researches on, 195.
—— carbon, 148, 156.
—— damp, 165.
—— dry iron, 165.
—— gas liberated from, 166, 167.
—— (iron) at high temperatures, 169, 170.
—— pure iron, 112–115.
—— residues soluble in hydrochloric acid, 162.
—— separation of, 157, etc.
Carbon, 144, 148, *et passim*.
—— amorphous, 148, 154.
—— and manganese, 245.
—— and steel, micrographical composition of, 132, 135.
—— carbide, 148.
—— combined, 156, 175.
—— content of martensite, 227, 232.
—— crystallisation of, 149.
—— disulphide, 40.
—— graphitic tempering, 154.
—— hardening, 148, 149.
—— in iron alloys, chemical composition of, 223.
Carbon, its proportion in varieties of iron, 145.
—— pure, 148.
—— (tempering), 100, 106, 148, etc.
—— steel, 111.
Carboniferous iron treated with nitric acid, 190.
Cast iron, 83.
Cavities with rough surface, 100, 103 (Plate IV. Figs. 40–43).
—— with smooth surface, 100–103.
Cement and hardening carbon distinguished, 195.
—— for iron, 84.
—— steel, 146.
—— steel, researches on, 112.
Cementite, 100, 111, 121, 123, 157.
—— chromiferous, 111.
—— curve of deposition of, 235.
"Chalypite," 172.
Charcoal and iodine solution, 43.
Chemical analysis, 2, 3.
—— analysis as an aid to micrography, 93, 94.
—— composition of slag, 289.
—— composition of the carbon present in iron alloys, 223.
Chloral hydrate dissolved in acetic acid, 40.
Chrome steel, 111.
Chromiferous cementite, 111.
Chromium, 144.
—— in iron alloys, 271.
Clausius' formula, 28.
Cobalt, 144.
"Coefficient of diffusion," 65.
"Coefficient of distribution" of substance, 64.
Coefficient of solubility of a gas, 45.
"Cohenite," 170–172.
Cold-short grades of iron, 257.
Coloration of iron, 91.
—— of steel, 91.
—— of surfaces of metals for micrography, 85, 89.
Composition of aluminates, 309.
—— of martensite, 231.
—— of silicate slags, 303.
—— of steel used in experiments for carbon separation, 164, 165.
Concentration, volumetric, 57.
Concentrated solutions, 7–9.
—— solutions, vapour tension of, 33.
Concretionary structure, 98.
Conductivity, metallic, 71, etc.
Constituents of iron, 237.
—— of slag, 298.
—— of Thomas slag, 319.
Conversion point of mixed crystals, 236.

Conversion points, 242.
Cooling curve for tin, 58 (Fig. 27).
—— of electrolytic iron, 238.
—— of solid iron-carbon alloys, 235 (Fig. 82).
—— of solutions, 7, 8, etc.
Copper, 95, 144.
Copper-aluminium alloys, 77 (Figs. 29 and 30).
Copper-antimony alloys, 77 (Figs. 29 and 30).
Copper and lead alloys, 97, 98.
—— and silver alloys, 95.
—— and tin alloys, 98.
—— chloride, 63.
—— in iron alloys, 272.
—— sulphate, 63.
Cryohydrates or mother liquors, 10.
Crystalline solid bodies, 57.
—— white iron, 83, 93.
Crystallisation of carbon, 149.
—— of metals seen with microscope, 95.
—— of tin, 58 (Fig. 27).
—— spontaneous, 60.
Crystals and grains distinguished, 95.
—— mixed, conversion point, 236.
—— mixed, solidification point, 236.
Cuprous oxide, 97.
Curve of deposition of cementite, 235.
Curves of solution of iron-carbon alloys, 223 (Plate X. Fig. 82).

DALTON'S law as to solutions of gases, 45.
De Benneville's researches on manganese, 246–250.
Definition of siderology, 1, 2, 3.
De Koninck's conclusions as to iron alloys, 186, 189.
δ-iron, 244.
Depositions, internal, in solid solutions, 54.
Detonation experiments, 167.
Diphenyl, 40.
Diphenylmethane, 40.
Depression in temperature of deposition, 225.
—— of solidification point of solution, 39.
Diamond, 148, 155.
—— steel, 268.
Dielectrical constant, 41.
Diffusibility of one metal in another, measurements of, 68.
"Diffusion," 65.
Dilute solutions, behaviour of, 7–9.
—— solutions, vapour tension of, 25–33.
Dimensions, molecular, measurement by osmotic pressure, 38.
Dissociation, power of, 40.
Dissolved carbon, equation for molecules of, 226.
Distillation, isothermal, 27.
"Distribution, coefficient of," 64.
Donath's experiments on combined carbon, 177, 179, 181.
Double salts, 63.
Drawing of metals, 97.
Dry grinding, 84.

EGGERTZ'S normal wire, 214, 215.
—— researches on combined carbon, 175.
—— test, 175, 193.
Electrical conductivity, 70.
—— graphite, 152, 153.
—— resistance, Le Chatelier's researches on, 243.
Electrolytes, 70.
Electrolytic iron, cooling of, 238.
Enamel slags, 301.
Enstatite, 138.
—— in slags, 299.
Equation for molecules of dissolved carbon, 226.
—— of condition, van der Waal, 56.
Equations for calculation of slags, 310.
—— determining weight by means of depression of solidification point of a solution, 39.
Etch-polishing, 121.
Etching surfaces of metals for micrography, 85–89.
—— with dilute nitric acid, 86.
—— with fused calcium chloride, 89.
—— with hydrochloric acid, 87.
—— with iodine tincture, 88.
Ether, 40.
Ethyl or methyl alcohol and water, vapour tension of, 32, 33.
Ethylene bromide, 40.
Eutectic alloy, 16.
—— mixtures, 10, 18.
—— solutions, 10.
Evaporation, latent heat of, 56.
—— of a liquid, 55.
Expansion, thermal, 76.
Experiments for separation of carbide, 157, etc.

FAYALITE, 139, 301 (Plate IX. Fig. 72).
Ferric chloride, hydrates of, 11, 12 (Plate I. Fig. 2).
—— oxide, 138.

Ferrite, 100, 107–111, 121, 123, 132, etc.
Ferro-aluminium, 99.
Ferro-chrome, 83, 99.
Ferro-manganese, 93, 99, 145, 146, 246, etc.
—— Hogg's researches on, 250–252.
Ferro-tungsten, 83, 93.
Ferrous oxide, 301, 326.
FeO-silicates, fusion of, 297 (Plate X. Figs. 90 and 91).
Fibrous structure, 99.
Fick's law, 65.
Finery iron, 146.
—— steel, 146.
Fireproof materials related to slags, 332.
Flat polishing, 84, 85.
Flexion as a test for hardness, 92 (Plate III. Figs. 31 and 32).
Forge iron, 145.
Forging of metals, 97.
Formation and fusion of slags, temperatures of, 296.
—— of slags, temperatures of, 293.
Formic acid and water, vapour tension of, 31, 33.
Formula of Clausius, 28.
Forsterite, 139.
Fractional analysis of iron, 93.
Fracture, intracrystalline, 110.
—— intragranular, 110.
Frictional resistance, calculation of, 66.
Furnace iron, 146.
—— slag, basic Martin, 322, 323.
Fusing point of an alloy, 14.
—— point of iron, 224.
—— temperatures of slags, 293.
Fusion of FeO-silicates, 297 (Plate X. Figs. 90 and 91).
—— of iron-calcium silicates, 297 (Plate X. Figs. 90 and 91).
—— of solids, latent heat of, 224.

γ-IRON, 237.
Gas bubbles, 100–103.
—— coefficient of solubility, 45.
—— liberated from carbide, 166, 167.
Gaseous mixture in molten iron and steel, 284.
—— products of iron alloys dissolved in acids, 213.
Gases and solutions, relation between, 22.
—— escaping during filling of mould, 278–283.
—— in iron alloys, 274.
—— in iron alloys, Fr. C. G. Müller's researches on, 275, 276.
Gases in iron alloys, Troost and Hautefeuille's researches on, 275.
—— in steel, Zyromski's researches on, 277.
—— liberation of, in cooling iron and steel, 284.
—— solutions of, 45, etc.
Gay-Lussac's law, 21, 23.
Geology, 2, 3.
Gehlenite, 140, 298, 306.
Gold and tin, alloy of, 35.
—— dissolved in bismuth, 68.
—— dissolved in lead, 68.
—— dissolved in tin, 68.
Grains and crystals distinguished, 95.
Granular structure (grey iron), 98.
Graphite, 100, 105 (Plate V. Fig. 45; Plate VI. Figs. 46, 47, 48), 123–127, 148, 150, 152, etc.
—— blast-furnace, 152.
—— electrical, 152, 153.
—— hydrate, 176.
—— natural, 152.
—— oxide, 152.
—— specific gravity of, 151.
—— specific head of, 151.
Graphitic acid, 152.
—— tempering carbon, 154.
Graphitite, 152.
Gredt's temperatures of formation and fusion of slags, 296.
Grey iron (granular structure), 98.
—— microscopical investigation of, 124.
Grey pig iron, 145, 146.
Grinding, dry, method of, 84.

HAMMERING of metals, 97.
Hardening and carbide carbon, author's researches on, 195.
—— and cement carbon distinguished, 195.
—— carbon, 148, 149, 172.
"Hardening" or "injurious" phosphorus, 266.
"Hardenite," 117, 173.
Hausmannite, 143.
Heat (specific) of alloys, 80.
Henry's law, 45.
Hercynite, 141.
Hexagonal prisms in phosphate slags, 320.
Heycock and Neville's equation, 226, 234, 334.
Hilgenstock's researches on slags, 312–316.
Hogg's researches on combined carbon, 203, 204, 209.

Hogg's researches on ferromanganese, 250–252.
—— researches on iron alloys, 184.
Hydrates of ferric chloride, 11, 12 (Plate I. Fig. 2).
—— of phosphate slags, 317.
—— of silica, 291.
Hydrocarbon from carbide carbon, 149.
Hydrochloric acid (aqueous solution) as a conductor, 70.
—— acid gas (pure) as a conductor, 70.
—— acid for etching, 87.
Hydrogen, 144.
—— and iron, relation between, 287.
—— in iron, Roberts-Austen's researches on, 286 (Fig. 85).
—— metals showing an affinity for, 288.
—— retained in cold iron and steel, 284.
Hydrographite oxide, 153.

Inclusions, slag, 100, 104 (Plate IV. Fig. 44).
Increase by cooling in tensile strength of iron, 238.
Interior of grains, shaly structure, 96.
"Internal pressure," 56.
—— separations or depositions in solid solutions, 54.
Intracrystalline fracture, 110.
Intragranular fracture, 110.
Iodine and charcoal solution, 43.
—— tincture for etching, 88.
"Ions" or molecules, 70.
Ingot iron, 145, 146, 262, 256.
—— steel, 145, 146.
"Injurious" or "hardening" phosphorus, 266.
Iron and hydrogen, relation between, 287.
—— allotropic forms of, 237.
—— alloys, chemical composition of, 144.
—— alloys dissolved in acids, gaseous products of, 213.
—— Bessemer, 146.
—— Blooming, 146.
——-calcium silicates, fusion of, 297 (Plate X. Figs. 90 and 91).
—— carbide, 148.
—— carbide at high temperatures, 169, 170.
—— carbide treated with acids, 168.
——-carbon alloys, cooling of, 235 (Fig. 82).
——-carbon alloys, curves of solution, 223 (Plate X. Fig. 82).
Iron, cast, 83.
—— coloration of, 91.
—— constituents of, 237.
—— crystalline white, 83, 93.
—— finery, 146.
—— forge, 145.
—— furnace, 146.
—— fusing point of, 224.
—— grey, 124.
—— grey (granular structure), 98.
—— ingot, 145, 146, 256, 262.
—— manganese, 246.
—— meteoric, 170.
——-olivine, 139.
—— ore, specular, 143.
—— pig, *passim*.
—— puddled, 146, 256, 262.
—— radial white (microlithic felt), 99.
—— refinery, 256.
—— reverberatory furnace, 146.
—— Siemens-Martin Pernot, 146.
—— silicide, 254.
—— telluritic, 172.
—— Thomas, 146.
—— welded, 145, 264.
—— welding wrought, 145.
—— white, 126.
—— white (paving-stone structure), 98.
—— wire from Bofors, 214, 215.
Isomorphic mixtures, 18.
Isomorphous salts, 63.
Isothermal distillation, 27.

Kathions, 70.

Latent heat of evaporation, 56.
—— heat of fusion of solids, 224.
Lead and copper alloys, 97.
—— dissolved in tin, 68.
—— nitrate, 63.
Le Chatelier on electrical resistance, 243.
Le Chatelier's researches on allotropic forms, 241.
Ledebur on slags, 289.
Liberation of gases in cooling iron and steel, 284.
Liebenow's theory of metallic conduction, 72, 73.
Lime, fusion of silicates of, 296 (Plate X. Figs. 86–89).
Liquefaction of a gas, 55.
Liquid eutectic alloy, solidification curve of, 231 (Fig. 82).
—— mercury as an alloy, 74.
—— solutions, Raoult's law for, 54.
—— supercooling of, 60.
Litharge, 242.

Locomotion of molecules, powers of, 56.

Magnesia and lime, fusion of silicates of, 296 (Plate X. Figs 86–89).
—— pyroxene, 138.
Magnetism of sub-carbide, 174.
Magnetite, 139 (Plate IX. Fig. 73), 141, 301.
Manganese, 146, 245, *et passim*.
—— combined with carbon, 245.
—— De Benneville's researches on, 246–250.
—— iron, 246.
—— Moissan's researches on, 252.
—— Osmond's researches on, 252.
—— oxide, 326.
—— steel, 122, 246.
—— sulphate, solution of, 10.
—— Troost's and Hautefeuille's researches on, 252.
Manganese-olivine, 139 (Plate IX. Fig. 74.
Manganoferrite, 143.
Martensite, 100, 115, 121, 123, 130, etc.
—— carbon content of, 227, 232.
—— composition of, 231.
—— saturation point, 228.
Martin furnace, slag (basic), 322, 323.
—— steel, 268.
Massicot, 242.
Measurement of weight by depression of vapour tension, 39.
Measurements of diffusibility of one metal into another, 68.
Melilite, 140.
—— in slags, 300.
Melilite-Scapolite group of minerals in slag, 140.
Mellithic acid, 153.
Melting and vaporisation, similarity between, 58, etc.
Mercury (liquid) as an alloy, 74.
Metal, motility of molecules, 66.
Metallic alloys, 2.
—— conductivity, 71, etc.
Metallography, 2.
—— anatomico-histological, 82.
—— biological, 82.
—— pathological, 82.
Metals, micrography of, 81.
—— opacity of, 74.
—— showing an affinity for hydrogen, 288.
—— surface suitable for micrography, 83.
Metasilicates in slags, 297.
Meteoric iron, 170.
Method of fractional analysis, 93.
Mica, 141.
Micrographical composition of steel with carbon, 132, 135.
Micrography of metals, 81.
Microlithic felt (radial white iron), 99.
Microliths, 98.
Microstructure of slags, 137.
"Missing carbon," 203.
Mixtures, eutectic, 10, 18.
—— isomorphic, 18.
Moissan's researches on manganese, 252.
Molecular depression of transformation point, 233.
—— theory of solution of gas in liquid, 46.
—— weight and osmotic pressure, 38.
Molecules of dissolved carbon in liquid steel and pig iron, equation for, 226.
—— mutual attraction of, 55.
—— powers of locomotion of, 56.
Molten alloys, 14.
—— iron and steel, gaseous mixture in, 284.
—— iron carbide, Saniter's analysis, 232.
Molybdenum, 144.
—— in iron alloys, 272.
Monoclinic crystals (blue) in phosphate slags, 320, 321.
Monticellite, 139.
Mother liquors or cryohydrates, 10.
Motility of molecules of metal, 66.
Mould, gases escaping during filling of 278–283.
Muirhead's analysis of blast-furnace slag, 308.
Müller, Fr. C. G., on gases in iron alloys, 275, 276.
Müller's researches on gases escaping during filling of mould, 278–283.
Mutual attraction of molecules, 55.

Natural graphite, 152.
Nickel, 144.
—— in iron alloys, 372.
—— steel, 122.
Nitrates of alkali metals, 63.
Nitric acid (dilute) for etching, 86.
—— acid, its effect on carboniferous iron, 190.
Nitrogen, 144.
—— in iron, 288.
Nitrographitoic acid, 179.

Octahedral sulphur, 241.
Olivine, calcareous, 139.

Olivine, group of minerals in slag, 139 (Plate IX. Figs. 71–74).
—— in slags, 300.
—— iron, 139.
—— manganese, 139 (Plate IX. Fig. 74.
—— (true), 139.
Opacity of metals, 74.
Osmond and Werth's researches, 182, 183.
Osmond's austenite points, 230.
—— recalescence curve, 239 (Plate X. Fig. 83).
—— researches on manganese, 252.
Osmotic pressure, 19.
—— pressure and molecular weight of dissolved substance, 38.
—— pressure of a solution proportional to its concentration, 21.
—— pressure, relation with other properties of solutions, 25, etc.
—— pressure varies as the temperature, 21.
Oxide, ferric, 138.
—— graphite, 153.
—— hydrographite, 153.
—— pyrographite, 153.
—— slags, 290, 329.
Oxygen in iron alloys, 144, 272.
—— in silica, 303.

Palladium, hydrogen dissolved in, 53.
Pathological metallography, 82.
Paving-stone structure (white iron), 98.
Pearlite, 100, 118 (Plate VIII. Figs. 56, 57), 121, 123, 133.
—— granular, 119.
—— scaly or lamellar, 118.
Peltier effects in alloys, 73.
Phenol, 40.
"Phenomena of adsorption," 43.
Phosphate and phosphide, 257.
—— slags, 317.
—— slags, blue monoclinic crystals in, 320, 321.
—— slags, hexagonal prisms in, 320.
—— slags, hydrates of, 317.
—— slags, rhombic plates in, 320, 321.
Phosphatic slags, 290.
Phosphide and phosphate of iron, 257.
"Phosphide" phosphorus, 266.
Phosphoric acid, retrogradation of, 321.
Phosphorus, 144, 151.
—— author's researches on, 258–267.
—— in iron alloys, 256.
Pig iron, *passim*.
Platinum dissolved in lead, 68.
Pleonast, 141.
Polishing, relief, 121.
Polishing surfaces of metals, 84.
Polymerisation, 111.
Potassium nitrate, 63.
Pressure and weight of dissolved substance, 38, etc.
—— osmotic, 19.
Princep's alloys, temperatures determined with, 293.
Prismatic sulphur, 241.
Products, Bessemer, 278.
—— Thomas, 281.
Properties of solutions, their relation to osmotic pressure, 25.
Proportion of carbon in iron, 145.
Propyl alcohol and water, vapour tension of, 32, 33.
Prost's researches on iron alloys, 185, 188, 189.
Puddled iron, 146, 256, 262.
Puddling slag, 325.
Pyrographite oxide, 153.
Pyroxene group of animals in slag, 137.
—— magnesia, 138.

Radial agglomerations, 98.
—— white iron (microlithic felt), 99.
Raoult's law for liquid solutions, 54.
Recalescence curve of Osmond, 239 (Plate X. Fig. 83).
—— points, 131.
Refinery iron, 256.
—— slags, 301.
Relation between gases and solutions, 22.
—— between iron and hydrogen, 287.
Relief polishing, 84, 85, 121.
Resistance to scratching, 91, 92.
"Retrogradation" of phosphoric acid, 321.
Reverberatory furnace iron, 146.
—— furnace steel, 146.
Rhodium dissolved in lead, 68.
Rhodonite, 139.
—— in slags, 299.
Rhombic plates in phosphate slag, 320, 321.
Riecke's formula, 66.
Roberts-Austen's researches on hydrogen in iron, 286 (Fig. 85).
—— researches on temperature at which diffusion occurs, 67 (Fig. 28).
Rolling on metals, effects of, 97.
Roozeboom's researches on mixed crystals, 236.
Rothmund's formula for molecular dimensions of dissolved carbon, 333.
—— law for solid solutions, 54.

Salts, double, 63.
—— isomorphous, 63.
Saniter's analysis of molten iron carbide, 232.
—— table for combined carbon, 206.
Saturation point of carbon for iron, 133.
—— point in martensite, 228.
Saccharose, 21, 66.
Sauveur's exposure of Arnold's tensile tests, 240 (Plate X. Fig. 84).
—— tables for combined carbon, 207, 208.
Scaly or lamellar pearlite, 118.
Schützenberger and Bourgeois' researches on combined carbon, 176, 177, 179, 180.
Scratching, resistance to, 91, 92.
Seger cone, temperatures determined with, 294, 295.
Separation of carbide, 157, etc.
Shaly interior of grains, 96.
Siderography, its definition, 1, 2, 3.
Siemens-Martin carbon steel, 146.
—— Pernot iron, 146.
Silica, 254, etc.
—— hydrates of, 291.
—— oxygen in, 303.
Silicate slags, 290, 303.
Silicic acid, 291.
Silicides, 254, etc.
Silicon, 144, 150, 157.
—— in iron alloys, 254, etc.
Silver-copper alloys, 14 (Plate I. Fig. 3), 95.
Silver dissolved in tin, 68.
—— solidification of, 15.
—— sulphide, 97.
Slag (blast-furnace) analysed by Muirhead, 308.
—— chemical composition of, 289.
—— constituents of, 298.
—— constituents soluble in HCl and HF, 308.
—— inclusions, 100, 104 (Plate IV. Fig. 44).
Slags as solutions, 289.
—— basic, 301.
—— constitution of, 7.
—— equations for calculation of, 310.
—— fusing temperatures of, 293.
—— Hilgenstock's researches on, 312–316.
—— in metal silicates, 297.
—— in relation to fireproof materials, 332.
—— microstructure of, 137.
—— oxide, 290.
—— phosphatic, 290.
—— refinery, 301.
Slags, silicate, 290.
—— Vogt's researches on, 298, 312, etc.
—— Vogt's table of, 142 (Fig. 79).
Sodium chlorate, 63.
—— sulphate, 63.
—— tartrate, 21.
Solid bodies, amorphous properties of, 57.
—— bodies, crystalline properties of, 57.
—— solutions, 48, etc.
—— solutions, Rothmund's law for, 54.
—— solutions with internal depositions, 54.
Solidification curve of the liquid eutectic alloy, 231 (Fig. 82).
—— of silver, 15.
—— point of a solution, depression of, 39.
—— point of mixed crystals, 236.
Solids, latent heat of fusion of, 224.
—— vapour tension of, 29.
Solubility, theory of, 55, etc.
—— of an alloy, 14.
Solution, aqueous, 7.
—— curves as basis for deduction of weight, 233.
—— of antimony in tin, 53.
—— of carbon in iron, 129 (Fig. 58).
—— tension of, 61.
Solutions and gases, relations between, 22.
—— concentrated, 7, 9.
—— concentrated, vapour tension of, 33.
—— cooling of, 7, 8, etc.
—— dilute, 7, 9.
—— dilute, vapour tension of, 25–33.
—— different varieties of, 16, 17.
—— eutectic, 10.
—— of gases, 45, etc.
—— solid, 48, etc.
—— slags as, 289.
—— supersaturated, 61.
—— their properties related to osmotic pressure, 25, etc.
—— with only one volatile constituent, 25 (Plate I. Fig. 15).
—— with two volatile constituents, 25, 31.
Solvent, vapour tension of, 25.
Sorbite, 100, 119, etc.
Specific gravity of graphite, 151.
—— heat of alloys, 80.
—— heat of graphite, 157.
Specular iron ore, 143.
Spiegeleisen, 146, 177, 267, 268.

Spiegeleisen, figures on, 89–91, 102 (Plate IV. Fig. 38).
Spinel, 141.
—— in slags, 301, 306.
—— zinc, 141.
Spontaneous crystallisation, 60.
Stalky structure of iron alloys, 99.
Steel, 262.
—— acid Bessemer, 267.
—— and carbon, micrographical composition of, 132, 135.
—— annealed, 116.
—— basic Bessemer, 267.
—— Bessemer, 146.
—— burnished, 146.
—— carbon, 111.
—— cement, 146.
—— cement, researches on, 112.
—— coloration of, 91.
"—— diamond," 268.
—— finery, 146.
—— ingot, 145, 146.
—— manganese, 122, 246.
—— Martin, 268.
—— nickel, 122.
—— reverberatory furnace, 146.
—— scorched, bubbles on, 103 (Plate IV. Fig. 39).
—— Siemens-Martin carbon, 146.
—— welded, 145, 146.
—— white, 146.
Stöchiometric conditions, 10.
Subcarbide, 173.
Sugar solutions, 21.
Sulphur, 144.
—— in iron alloys, 270.
—— octahedral, 241.
—— prismatic, 241.
Supercooling of liquid, 60.
Supersaturated solutions, 61.
Surface of metals suitable for micrography, 83.
Surfaces, etching for micrography, 85–89.
—— of metals, coloration of micrography, 85, 89-91.

TELLURITIC iron, 172.
Tempering carbon, 148.
—— carbon, graphitic, 154.
Temperature of conversion, 242.
—— of deposition, depression in, 225.
Temperatures of formation and fusion of slags, 296.
—— of formation of slags, 293.
—— of slags determined with Princep's alloys, 293.
—— of slags determined with Seger cone, 294, 295.
Tensile strength of iron increased by cooling, 238.
—— tests by Sauveur refuting Arnold, 240 (Plate X. Fig. 84).
"Tension of solution," 61.
Tephroite, 139.
Thermal expansion, 76.
Thiophene dissolved in benzol, 53.
Thomas iron, 146.
—— products, 281.
—— slag, constituents of, 319, 325.
Tin, 144.
—— and bismuth, alloys of, 42.
—— and gold, alloy of, 35.
—— crystallisation of, 58 (Fig. 27).
Titanium, 144.
—— in iron alloys, 272.
Transformation point, molecular depression of, 233.
Troostite, 100, 121.
Troost and Hautefeuille on gases in iron alloys, 275.
Troost's and Hautefeuille's researches on manganese, 252.
Truss-iron, 146.
Tungsten, 144, 157.
—— borate, 271.
—— in iron alloys, 272.

VANADIUM, 144.
Van der Waal's equation for Boyle's and Gay-Lussac's laws, 23.
—— equation of condition, 56.
Van't Hoff's equation, 225.
Vaporisation and melting, similarity between, 58, etc.
Vapour tension of concentrated solutions, 33.
—— tension of dilute solutions, 25–33.
—— tension of ethyl or methyl alcohol and water, 32, 33.
—— tension of formic acid and water, 31, 33.
—— tension of propyl alcohol and water, 32, 33.
—— tension of solids, 29.
—— tension of solutions with two volatile constituents, 31.
—— tension of solvent, 25.
Volume of alloys, 79.
Volumetric concentration, 57.
Vogt's researches on slags, 137, 298, 312, etc.
—— table of slags, 142 (Fig. 79).
Von Jüptner's deductions on combined carbon, 210, 211, 212.
—— researches on hardening and carbide carbon, 195.

Von Jüptner's researches on phosphorus, 258–267.

Weight determined from curves of solution, 233.
—— measured by depression of vapour tension, 39.
Welded iron, 145, 264.
—— steel, 145, 146.
Welding wrought iron, 145, 146.
White iron (paving-stone structure), 98, 126.
White iron, radial (microlithic felt), 99.
—— pig iron, 145, 146.
—— steel, 146.
Willemite, 141.
Wire, Eggertz's normal, 214, 215.
Wollastonite, 139.
—— in slags, 299.
Wrought iron, welding, 145, 146.

Zinc, 144.
—— spinel, 141.
Zyromski on gases in steel, 277.

PRINTED BY MORRISON AND GIBB LIMITED, EDINBURGH

JULY, 1902.

Catalogue

OF

SCOTT, GREENWOOD & CO.'S

Special Technical Works

FOR

MANUFACTURERS, PROFESSIONAL MEN, STUDENTS, COLLEGES AND TECHNICAL SCHOOLS

BY EXPERT WRITERS

INDEX TO SUBJECTS.

	PAGE
Agricultural Chemistry	4
Air, Industrial Use of	10
Alum	4
Alumina Sulphates	4
Ammonia	5
Aniline Colours	6
Animal Fats	2
Anti-corrosive Paints	3
Architectural Pottery	17
Artificial Perfumes	7
Balsams	11
Bleaching	26
Bone Products	11
Brick-making	
Burnishing Brass	31
Carpet Yarn Printing	17
Ceramic Books	16-20
Charcoal	11
Chemical Essays	8
Chemistry of Pottery	20
Clay Analysis	17
Coal-dust Firing	30
Colour Matching	27
Colliery Recovery Work	29
Colour-mixing for Dyers	27
Colouring Pottery	17
Colour Theory	24
Combing Machines	29
Compounding Oils	2
Condensing Apparatus	14
Cosmetics	7
Cotton Dyeing	28
Cotton Spinning	28, 29
Dampness in Buildings	35
Decorating Pottery	17
Decorators' Books	32
Decorative Textiles	22
Dictionary of Paint Materials	9
Drying Oils	7
Drying with Air	14
Dyeing Marble	35
Dyeing Woollen Fabrics	28
Dyers' Materials	25
Enamelling Metal	21, 22, 32
Enamels	21
Essential Oils	7
Evaporating Apparatus	14
External Plumbing	30
Fats	2, 3
Gas Firing	30
Glass-making Recipes	16
Glass Painting	19
Glue Making	11
Glue Testing	8
Greases	2, 4
History of Staffs Potteries	20
Hops	33
Hot-water Supply	32
India-Rubber	13
Inks	7
Iron-corrosion	3
Iron, Science of	36
Japanning	32
Lacquering	31
Lake Pigments	6, 10
Lead and its Compounds	12
Lead Ores	13
Leather Industry	15
Leather-working Materials	14
Lubricants	2, 4
Lubricating Oils	4
Manures	4, 11
Mineral Pigments	10
Oil and Colour Recipes	10
Oil Boiling	5
Oil Refining	5
Oils	2, 4, 7
Ozone, Industrial Use of	10
Painters' Books	32
Painting Glass	19
Paint Manufacture	12
Paint Materials	6, 9
Paint-material Testing	6
Paper-pulp Dyeing	21
Petroleum	8
Pigments, Chemistry of	12
Plumbers' Work	30, 31
Porcelain Painting	19
Pottery Clays	19
Pottery Manufacture	16, 18
Pottery Recipes	16
Power-loom Weaving	23
Preserved Foods	34
Recipes for Oilmen, etc.	10
Resins	11
Risks of Occupations	13
Rivetting China, etc.	19
Rontgen Ray Work	13
Scheele's Essays	8
Silk Dyeing	27
Smoke Prevention	30
Soaps	2
Spinning	28
Staining Marble, Bone, etc.	35
Steam Drying	14
Sweetmeats	34
Terra-cotta	17
Testing Paint Materials	6
Testing Yarns	22
Textile Fabrics	22-29
Textile Materials	24
Timber	34
Varnishes	5
Vegetable Fats	3
Waste Utilisation	5
Water, Industrial Use of	10
Wood	33, 34
Wood Waste Utilisation	33
Wood Dyeing	35
Wool Dyeing	27
X-Ray Work	13
Yarn Numbering	23
Yarn Testing	22

SCOTT, GREENWOOD & CO.,

19 LUDGATE HILL, LONDON, E.C.

Tel. Address: "PRINTERIES, LONDON". **Tel. No. 5403, Bank.**

Books on Oils, Soaps, Colours, Chemicals, Glue, Varnishes, etc.

THE PRACTICAL COMPOUNDING OF OILS, TALLOW AND GREASE FOR LUBRICATION, ETC.

By AN EXPERT OIL REFINER. 100 pp. 1898. Demy 8vo. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., **Introductory Remarks** on the General Nomenclature of Oils, Tallow and Greases suitable for Lubrication.—II., **Hyrocarbon Oils.**—III., **Animal and Fish Oils.**—IV., **Compound Oils.**—V., **Vegetable Oils.**—VI., **Lamp Oils.**—VII., **Engine Tallow, Solidified Oils and Petroleum Jelly.**—VIII., **Machinery Greases: Loco and Anti-friction.**—IX., **Clarifying and Utilisation of Waste Fats, Oils, Tank Bottoms, Drainings of Barrels and Drums, Pickings Up, Dregs, etc.**—X., **The Fixing and Cleaning of Oil Tanks, etc.**—**Appendix and General Information.**

Press Opinions.

"This work is written from the standpoint of the oil trade, but its perusal will be found very useful by users of machinery and all who have to do with lubricants in any way."—*Colliery Guardian.*

"The properties of the different grades of mineral oil and of the animal and vegetable non-drying oils are carefully described, and the author justly insists that the peculiarities of the machinery on which the lubricants are to be employed must be considered almost before everything else. . . . The chapters on grease and solidified oils, etc., are excellent."—*The Ironmonger.*

SOAPS. A Practical Manual of the Manufacture of Domestic, Toilet and other Soaps.

By GEORGE H. HURST, F.C.S. Illustrated with Sixty-six Engravings. 390 pp. 1898. Price 12s. 6d.; India and Colonies, 13s. 6d.; Other Countries, 15s.; strictly net.

Contents.

Chapters I., **Introductory.**—II., **Soap-maker's Alkalies.**—III., **Soap Fats and Oils.**—IV., **Perfumes.**—V., **Water as a Soap Material.**—VI., **Soap Machinery.**—VII., **Technology of Soap-making.**—VIII., **Glycerine in Soap Lyes.**—IX., **Laying out a Soap Factory.**—X., **Soap Analysis.**—**Appendices.**

Press Opinions.

"We think it is the most practical book on these subjects that has come to us from England so far."—*American Soap Journal.*

"Much useful information is conveyed in a convenient and trustworthy manner which will appeal to practical soap-makers."—*Chemical Trade Journal.*

"Works that deal with manufacturing processes, and applied chemistry in particular, are always welcome. Especially is this the case when the material presented is so up-to-date as we find it here."—*Bradford Observer.*

ANIMAL FATS AND OILS: Their Practical Production, Purification and Uses for a great Variety of Purposes.

Their Properties, Falsification and Examination. A Handbook for Manufacturers of Oil and Fat Products, Soap and Candle Makers, Agriculturists, Tanners, Margarine Manufacturers, etc., etc. By LOUIS EDGAR ANDÉS. Sixty-two Illustrations. 240 pp. 1898. Demy 8vo. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net.

Contents.

Introduction. Occurrence, Origin, Properties and Chemical Constitution of Animal Fats Preparation of Animal Fats and Oils. Machinery. Tallow-melting Plant. Extraction Plant. Presses. Filtering Apparatus. Butter: Raw Material and Preparation, Properties, Adulterations, Beef Lard or Remelted Butter, Testing. Candle-fish Oil. Mutton-Tallow. Hare Fat. Goose Fat. Neatsfoot Oil. Bone Fat: Bone Boiling, Steaming Bones, Extraction, Refining. Bone Oil. Artificial Butter: Oleomargarine, Margarine Manufacture in France, Grasso's Process, "Kaiser's Butter," Jahr & Münzberg's Method, Filbert's Process, Winter's Method. Human Fat. Horse Fat. Beef Marrow. Turtle Oil. Hog's Lard: Raw Material Preparation, Properties, Adulterations, Examination. Lard Oil. Fish Oils. Liver Oils. Artificial Train Oil. Wool Fat: Properties, Purified Wool Fat. Spermaceti: Examination of Fats and Oils in General.

Press Opinions.

"The descriptions of technical processes are clear, and the book is well illustrated and should prove useful."—*Manchester Guardian.*

"It is a valuable work, not only for the student, but also for the practical manufacturer of oil and fat products."—*Journal of the American Chemical Society.*

"The work is very fully illustrated, and the style throughout is in strong contrast to that employed in many such treatises, being simple and clear."—*Shoe and Leather Record.*

"An important handbook for the 'fat industry,' now a large one."—*Newcastle Chronicle.*

"The latest and most improved forms of machinery are in all cases indicated, and the many advances which have been made during the past years in the methods of producing the more common animal fats—lard, tallow and butter—receive due attention."—*Glasgow Herald.*

VEGETABLE FATS AND OILS: Their Practical Preparation, Purification and Employment for Various Purposes, their Properties, Adulteration and Examination. A Handbook for Oil Manufacturers and Refiners, Candle, Soap and Lubricating Oil Makers, and the Oil and Fat Industry in General. Translated from the German of LOUIS EDGAR ANDÉS. Ninety-four Illustrations. 340 pp. Second Edition. 1902. Demy 8vo. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net.

Contents.

Statistical Data. General Properties of the Vegetable Fats and Oils. Estimation of the Amount of Oil in Seeds. Table of Vegetable Fats and Oils, with French and German Nomenclature, Source and Origin and Percentage of Fat in the Plants from which they are Derived. The Preparation of Vegetable Fats and Oils: Storing Oil Seeds; Cleaning the Seed. Apparatus for Grinding Oil Seeds and Fruits. Installation of Oil and Fat Works. Extraction Method of Obtaining Oils and Fats. Oil Extraction Installations. Press Moulds. Non-drying Vegetable Oils. Vegetable drying Oils. Solid Vegetable Fats Fruits Yielding Oils and Fats. Wool-softening Oils. Soluble Oils. Treatment of the Oil after Leaving the Press Improved Methods of Refining with Sulphuric Acid and Zinc Oxide or Lead Oxide. Refining with Caustic Alkalies, Ammonia, Carbonates of the Alkalies, Lime. Bleaching Fats and Oils. Practical Experiments on the Treatment of Oils with regard to Refining and Bleaching. Testing Oils and Fats.

Press Opinions.

"Concerning that and all else within the wide and comprehensive connection involved, this book must be invaluable to every one directly or indirectly interested in the matters it treats of."—*Commerce.*

"A valuable and highly interesting book of reference."—*Manufacturing Chemist.*

IRON-CORROSION, ANTI-FOULING AND ANTI-CORROSIVE PAINTS. By LOUIS EDGAR ANDÉS. Sixty-two Illustrations. 275 pp. Translated from the German. Demy 8vo. 1900. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net.

Contents.

Iron-rust and its Formation—Protection from Rusting by Paint—Grounding the Iron with Linseed Oil, etc.—Testing Paints—Use of Tar for Painting on Iron—Anti-corrosive Paints—Linseed Varnish—Chinese Wood Oil—Lead Pigments—Iron Pigments—Artificial Iron Oxides—Carbon—Preparation of Anti-corrosive Paints—Results of Examination of Several Anti-corrosive Paints—Paints for Ship's Bottoms—Anti-fouling Compositions—Various Anti-corrosive and Ship's Paints—Official Standard Specifications for Ironwork Paints—Index.

Press Opinions.

"This is a very valuable book."—*Bristol Mercury.*

"Will be of great service to paint manufacturers, engineering contractors, ironfounders, shipbuilders and others."—*Engineer and Iron Trades Advertiser.*

"Deals with the subject in a manner at once practical and scientific, and is well worthy of the attention of all builders, architects and engineers."—*The Builder.*

"The book is very readable and full of valuable information."—*Railway Engineer.*

"The author goes fully into his subject."—*Journal of Gas Lighting.*

"The book is an exceedingly useful record of what has been done in connection with iron preservation, and will undoubtedly prove to be of much value to railway engineers, shipowners, etc."—*Fairplay.*

"Will be particularly useful to iron manufacturers, shipbuilders and shipowners. . . ."—*Ironmonger.*

". . . The book is a welcome contribution to technological literature."—*Western Daily Mercury.*

"The author has evidently thoroughly investigated and mastered the subject of iron-corrosion, its cause and its prevention."—*Iron and Steel Trades Journal.*

THE MANUFACTURE OF ALUM AND THE SULPHATES AND OTHER SALTS OF ALUMINA AND IRON. Their Uses and Applications as Mordants in Dyeing and Calico Printing, and their other Applications in the Arts, Manufactures, Sanitary Engineering, Agriculture and Horticulture. Translated from the French of LUCIEN GESCHWIND. 195 Illustrations. Nearly 400 pp. Royal 8vo. 1901. Price 12s. 6d.; India and Colonies, 13s. 6d.; Other Countries, 15s.; strictly net.

Contents.

Part I., **Theoretical Study of Aluminium, Iron, and Compounds of these Metals.**—Chapters I., Aluminium and its Compounds.—II., Iron and Iron Compounds.

Part II., **Manufacture of Aluminium Sulphates and Sulphates of Iron.**—Chapters III., Manufacture of Aluminium Sulphate and the Alums.—IV., Manufacture of Sulphates of Iron.

Part III., **Uses of the Sulphates of Aluminium and Iron.**—Chapters V., Uses of Aluminium Sulphate and Alums—Application to Wool and Silk—Preparing and using Aluminium Acetates—Employment of Aluminium Sulphate in Carbonising Wool—The Manufacture of Lake Pigments—Manufacture of Prussian Blue—Hide and Leather Industry—Paper Making—Hardening Plaster—Lime Washes—Preparation of Non-inflammable Wood, etc.—Purification of Waste Waters.—VI., **Uses and Applications of Ferrous Sulphate and Ferric Sulphates.**—Dyeing—Manufacture of Pigments—Writing Inks—Purification of Lighting Gas—Agriculture—Cotton Dyeing—Disinfectant—Purifying Waste Liquors—Manufacture of Nordhausen Sulphuric Acid—Fertilising.

Part IV., **Chemical Characteristics of Iron and Aluminium.—Analysis of Various Aluminous or Ferruginous Products.**—Chapter VII., Aluminium.—**Analysing Aluminium Products.**—Alunite Alumina—Sodium Aluminate—Aluminium Sulphate. Chapter VIII., **Iron.**—Analytical Characteristics of Iron Salts—Analysis of Pyritic Lignite—Ferrous and Ferric Sulphates—Rouge Mordant—Index.

MANUAL OF AGRICULTURAL CHEMISTRY. By HERBERT INGLE, F.I.C., Lecturer on Agricultural Chemistry, the Yorkshire College; Lecturer in the Victoria University. 388 pp. 11 Illustrations. 1902. Demy 8vo. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d. net.

Contents.

Chapters I., Introduction.—II., The Atmosphere.—III., The Soil.—IV., The Reactions occurring in Soils.—V., The Analysis of Soils.—VI., Manures, Natural.—VII., Manures (continued).—VIII., The Analysis of Manures.—IX., The Constituents of Plants.—X., The Plant.—XI., Crops.—XII., The Animal.—XIII., Foods and Feeding.—XIV., Milk and Milk Products.—XV., The Analysis of Milk and Milk Products.—XVI., Miscellaneous Products used in Agriculture.—Appendix.—Index.

LUBRICATING OILS, FATS AND GREASES: Their Origin, Preparation, Properties, Uses and Analyses. A Handbook for Oil Manufacturers, Refiners and Merchants, and the Oil and Fat Industry in General. By GEORGE H. HURST, F.C.S. Second Edition. Sixty-five Illustrations. 313 pp. Demy 8vo. 1902. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net.

Contents.

Chapters I., **Introductory.** Oils and Fats, Fatty Oils and Fats, Hydrocarbon Oils, Uses of Oils.—II., **Hydrocarbon Oils.** Distillation, Simple Distillation, Destructive Distillation, Products of Distillation, Hydrocarbons, Paraffins, Olefins, Napthenes.—III., **Scotch Shale Oils.** Scotch Shales, Distillation of Scotch Oils, Shale Retorts, Products of Distilling Shales, Separating Products, Treating Crude Shale Oil, Refining Shale Oil, Shale Oil Stills, Shale Naphtha Burning Oils, Lubricating Oils, Wax.—IV., **Petroleum.** Occurrence, Geology, Origin, Composition, Extraction, Refining, Petroleum Stills, Petroleum Products, Cylinder Oils, Russian Petroleum, Deblooming Mineral Oils.—V., **Vegetable and Animal Oils.** Introduction, Chemical Composition of Oils and Fats, Fatty Acids, Glycerine, Extraction of Animal and Vegetable Fats and Oils, Animal Oils, Vegetable Oils, Rendering, Pressing, Refining, Bleaching, Tallow, Tallow Oil, Lard Oil, Neatsfoot Oil, Palm Oil, Palm Nut Oil, Cocoanut Oil, Castor Oil, Olive Oil, Rape and Colza Oils, Arachis Oil, Niger Seed Oil, Sperm Oils, Whale Oil, Seal Oil, Brown Oils, Lardine, Thickened Rape Oil.—VI., **Testing and Adulteration of Oils.** Specific Gravity, Alkali Tests, Sulphuric Acid Tests, Free Acids in Oils, Viscosity Tests, Flash and Fire Tests, Evaporation Tests, Iodine and Bromide Tests, Elaidin Test, Melting Point of Fat, Testing Machines.—VII., **Lubricating Greases.** Rosin Oil, Anthracene Oil, Making Greases, Testing and Analysis of Greases.—VIII., **Lubrication.** Friction and Lubrication, Lubricant, Lubrication of Ordinary Machinery, Spontaneous Combustion of Oils, Stainless Oils, Lubrication of Engine Cylinders, Cylinder Oils.—**Appendices.** A. Table of Baume's Hydrometer—B. Table of Thermometric Degrees—C. Table of Specific Gravities of Oils—**Index.**

THE UTILISATION OF WASTE PRODUCTS. A Treatise on the Rational Utilisation, Recovery and Treatment of Waste Products of all kinds. By Dr. THEODOR KOLLER. Translated from the Second Revised German Edition. Twenty-two Illustrations. Demy 8vo. 280 pp. 1902. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Introduction.—Chapters I., The Waste of Towns.—II., **Ammonia and Sal-Ammoniac**—Rational Processes for Obtaining these Substances by Treating Residues and Waste.—III., Residues in the Manufacture of Aniline Dyes.—IV., Amber Waste.—V., Brewers' Waste.—VI., Blood and Slaughter-House Refuse.—VII., Manufactured Fuels.—VIII., Waste Paper and Bookbinders' Waste.—IX., Iron Slags.—X., Excrement.—XI., Colouring Matters from Waste.—XII., Dyers' Waste Waters.—XIII., Fat from Waste.—XIV., Fish Waste.—XV., Calamine Sludge.—XVI., Tannery Waste.—XVII., Gold and Silver Waste.—XVIII., India-rubber and Caoutchouc Waste.—XIX., Residues in the Manufacture of Rosin Oil.—XX., Wood Waste.—XXI., Horn Waste.—XXII., Infusorial Earth.—XXIII., Iridium from Goldsmith's Sweepings.—XXIV., Jute Waste.—XXV., Cork Waste.—XXVI., Leather Waste.—XXVII., Glue Makers' Waste.—XXVIII., Illuminating Gas from Waste and the By-Products of the Manufacture of Coal Gas.—XXIX., Meerschum.—XXX., Molasses.—XXXI., Metal Waste.—XXXII., By-Products in the Manufacture of Mineral Waters.—XXXIII., Fruit.—XXXIV., The By-Products of Paper and Paper Pulp Works.—XXXV., By-Products in the Treatment of Coal Tar Oils.—XXXVI., Fur Waste.—XXXVII., The Waste Matter in the Manufacture of Parchment Paper.—XXXVIII., Mother of Pearl Waste.—XXXIX., Petroleum Residues.—XL., Platinum Residues.—XLI., Broken Porcelain, Earthenware and Glass.—XLII., Salt Waste.—XLIII., Slate Waste.—XLIV., Sulphur.—XLV., Burnt Pyrites.—XLVI., Silk Waste.—XLVII., Soap Makers' Waste.—XLVIII., Alkali Waste and the Recovery of Soda.—XLIX., Waste Produced in Grinding Mirrors.—L., Waste Products in the Manufacture of Starch.—LI., Stearic Acid.—LII., Vegetable Ivory Waste.—LIII., Turf.—LIV., Waste Waters of Cloth Factories.—LV., Wine Residues.—LVI., Tinplate Waste.—LVII., Wool Waste.—LVIII., Wool Sweat.—LIX., The Waste Liquids from Sugar Works.—Index.

AMMONIA AND ITS COMPOUNDS: Their Manufacture and Uses. By CAMILLE VINCENT, Professor at the Central School of Arts and Manufactures, Paris. Translated from the French by M. J. SALTER. Royal 8vo. 113 pp. 1901. Thirty-two Illustrations. Price 5s.; India and Colonies, 5s. 6d.; Other Countries, 6s.; strictly net.

Contents.

Chapters I., **General Considerations:** Sections 1. Various Sources of Ammoniacal Products; 2. Human Urine as a Source of Ammonia. II., **Extraction of Ammoniacal Products from Sewage:** Sections 1. Preliminary Treatment of Excreta in the Settling Tanks—The Lencauchez Process, The Bilange Process, The Kuentz Process; 2. Treatment of the Clarified Liquors for the Manufacture of Ammonium Sulphate—The Figuera Process and Apparatus, Apparatus of Margueritte and Sourdeval, The Lair Apparatus, Apparatus of Sintier and Muhé, Apparatus of Bilange, The Kuentz Process, Process and Apparatus of Hennebutte and De Vauréal; 3. Treatment of Entire Sewage—Chevalet's Apparatus, Paul Mallet's Apparatus, Lencauchez's Apparatus. III., **Extraction of Ammonia from Gas Liquor:** Sections 1. Clarification of Gas Liquor; 2. Manufacture of Ammonium Sulphate—A. Mallet's Apparatus, A. Mallet's Modified Apparatus, Paul Mallet's Apparatus, Chevalet's Apparatus, Grüneberg's Apparatus; 3. Concentration of Gas Liquor—Solvay's Apparatus, Kuentz's Apparatus, Grüneberg's Apparatus. IV., **Manufacture of Ammoniacal Compounds from Bones, Nitrogenous Waste, Beetroot Wash and Peat:** Sections 1. Ammonia from Bones; 2. Ammonia from Nitrogenous Waste Materials; 3. Ammonia from Beetroot Wash (Vinasse); 4. Ammonia from Peat—Treatment of the Ammoniacal Liquors. V., **Manufacture of Caustic Ammonia, and Ammonium Chloride, Phosphate and Carbonate:** Sections 1. Manufacture of Caustic Ammonia: 2. Manufacture of Ammonium Chloride—From Fermented Urine, Process of the Lesage Company, Kuentz's Process; From Gas Liquor, English Process, Kuentz's Process; From the Dry Distillation of Animal Matter; From Ammonium Sulphate, Sublimation; 3. Ammonium Phosphates; 4. Carbonates of Ammonium—Sesquicarbonate from Animal Matter, English Process, Uses. VI., **Recovery of Ammonia from the Ammonia-Soda Mother Liquors:** Sections 1. General Considerations; 2. Apparatus of Schlœsing and Rolland: 3. Apparatus of the Société Anonyme de l'Est.—**Index.**

THE MANUFACTURE OF VARNISHES, OIL REFINING AND BOILING, AND KINDRED INDUSTRIES. Describing the Manufacture of Spirit Varnishes and Oil Varnishes; Raw Materials: Resins, Solvents and Colouring Principles; Drying Oils: their Properties, Applications and Preparation by both Hot and Cold Processes; Manufacture, Employment and Testing of Different Varnishes. Translated from the French of A. LIVACHE, Ingénieur Civil des Mines. Greatly Extended and Ad

to English Practice, with numerous Original Recipes by JOHN GEDDES MCINTOSH, Lecturer on Oils, Colours and Varnishes, Regent Street Polytechnic. Twenty-seven Illustrations. 400 pp. Demy 8vo. 1899. Price 12s. 6d.; India and Colonies, 13s. 6d.; Other Countries, 15s.; strictly net.

Contents.

I. Resins: Gum Resins, Oleo Resins and Balsams, Commercial Varieties, Source, Collection, Characteristics, Chemical Properties, Physical Properties, Hardness, Adulterations Appropriate Solvents, Special Treatment, Special Use.—II. Solvents: Natural, Artificial, Manufacture, Storage, Special Use.—III. Colouring: Principles, (1) Vegetable, (2) Coal Tar, (3) Coloured Resinates, (4) Coloured Oleates and Linoleates.—Gum Running: Furnaces, Bridges, Flues, Chimney Shafts, Melting Pots, Condensers, Boiling or Mixing Pans, Copper Vessels, Iron Vessels (Cast), Iron Vessels (Wrought), Iron Vessels (Silvered), Iron Vessels (Enamelled), Steam Superheated Plant, Hot-air Plant.—Spirit Varnish Manufacture: Cold Solution Plant, Mechanical Agitators, Hot Solution Plant, Jacketted Pans, Mechanical Agitators, Clarification and Filtration, Bleaching Plant, Storage Plant.—Manufacture, Characteristics and Uses of the Spirit Varnishes yielded by: Amber, Copal, Dammar, Shellac, Mastic, Sandarac, Rosin, Asphalt, India Rubber, Gutta Percha, Collodion, Celluloid, Resinates, Oleates.—Manufacture of Varnish Stains.—Manufacture of Lacquers.—Manufacture of Spirit Enamels.—Analysis of Spirit Varnishes.—Physical and Chemical Constants of Resins.—Table of Solubility of Resins in different Menstrua.—Systematic qualitative Analysis of Resins, Hirschop's tables.—Drying Oils: Oil Crushing Plant, Oil Extraction Plant, Individual Oils, Special Treatment of Linseed Oil Poppyseed Oil, Walnut Oil, Hempseed Oil, Llamantia Oil, Japanese Wood Oil, Gurjun Balsam, Climatic Influence on Seed and Oil.—Oil Refining: Processes.—Oil Boiling: Pale Boiled Oil, Double Boiled Oil, Hartley and Blenkinsop's Process.—Driers: Manufacture, Special Individual Use of (1) Litharge, (2) Sugar of Lead, (3) Red Lead, (4) Lead Borate, (5) Lead Linoleate, (6) Lead Resinate, (7) Black Oxide of Manganese, (8) Manganese Acetate, (9) Manganese Borate, (10) Manganese Resinate, (11) Manganese Linoleate, Mixed Resinates and Linoleates, Manganese and Lead, Zinc Sulphate, Terebine, Liquid Driers.—Solidified Boiled Oil.—Manufacture of Linoleum.—Manufacture of India Rubber Substitutes.—Printing Ink Manufacture.—Lithographic Ink Manufacture.—Manufacture of Oil Varnishes.—Running and Special Treatment of Amber, Copal, Kauri, Manilla.—Addition of Oil to Resin.—Addition of Resin to Oil.—Mixed Processes.—Solution in Cold of previously Fused Resin.—Dissolving Resins in Oil, etc., under pressure.—Filtration.—Clarification.—Storage.—Ageing.—Coachmakers' Varnishes and Japans.—Oak Varnishes.—Japanners' Stoving Varnishes.—Japanners' Gold Size.—Brunswick Black.—Various Oil Varnishes.—Oil-Varnish Stains.—Varnishes for "Enamels".—India Rubber Varnishes.—Varnishes Analysis: Processes, Matching.—Faults in Varnishes: Cause, Prevention.—Experiments and Exercises.

THE MANUFACTURE OF LAKE PIGMENTS FROM ARTIFICIAL COLOURS. By FRANCIS H. JENNISON, F.I.C., F.C.S. **Sixteen Coloured Plates, showing Specimens of Eighty-nine Colours, specially prepared from the Recipes given in the Book.** 136 pp. Demy 8vo. 1900. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., Introduction.—II., The Groups of the Artificial Colouring Matters.—III., The Nature and Manipulation of Artificial Colours.—IV., Lake-forming Bodies for Acid Colours.—V., Lake-forming Bodies' Basic Colours.—VI., Lake Bases.—VII., The Principles of Lake Formation.—VIII., Red Lakes.—IX., Orange, Yellow, Green, Blue, Violet and Black Lakes.—X., The Production of Insoluble Azo Colours in the Form of Pigments.—XI., The General Properties of Lakes Produced from Artificial Colours.—XII., Washing, Filtering and Finishing.—XIII, Matching and Testing Lake Pigments.—Index.

Press Opinions.

"Evidently the result of prolonged research. A valuable consulting work."—*Derby Mercury.*

"The practical portion of the volume is the one which will especially commend itself, as that is the part of the subject which most readers would buy the book for."—*Chemist and Druggist.*

"A very valuable treatise on the manufacture of lake pigments of the coal-tar series principally."—*Chemical Trade Journal.*

"This is undoubtedly a book which will occupy a very high place amongst technical works, and will prove of exceptional value to all whom it immediately concerns."—*Eastern Morning News.*

THE TESTING AND VALUATION OF RAW MATERIALS USED IN PAINT AND COLOUR MANUFACTURE. By M. W. JONES, F.C.S. A Book for the Laboratories of Colour Works. 88 pp. Crown 8vo. 1900. Price 5s.; India and Colonies, 5s. 6d.; Other Countries, 6s.; strictly net.

Contents.

Aluminium Compounds. China Clay. Iron Compounds. Potassium Compounds. Sodium Compounds. Ammonium Hydrate. Acids. Chromium Compounds. Tin Compounds. Copper Compounds. Lead Compounds. Zinc Compounds. Manganese Compounds. Arsenic Compounds. Antimony Compounds. Calcium Compounds. Barium Compounds. Cadmium Compounds. Mercury Compounds. Ultramarine. Cobalt and Carbon Compounds. Oils Index.

THE CHEMISTRY OF ESSENTIAL OILS AND ARTIFICIAL PERFUMES. By ERNEST J. PARRY, B.Sc. (Lond.), F.I.C., F.C.S. Illustrated with Twenty Engravings. 411 pp. 1899. Demy 8vo. Price 12s. 6d.; India and Colonies, 13s. 6d.; Other Countries, 15s.; strictly net.

Contents.

Chapters I., **The General Properties of Essential Oils.**—II., **Compounds occurring in Essential Oils.**—III., **The Preparation of Essential Oils.**—IV., **The Analysis of Essential Oils.**—V., **Systematic Study of the Essential Oils.**—VI., **Terpeneless Oils.**—VII., **The Chemistry of Artificial Perfumes.**—**Appendix**: Table of Constants.

Press Opinions.

"Will take a high place in the list of scientific text-books."—*London Argus.*

"We can heartily recommend this volume."—*British and Colonial Druggist.*

"Mr. Parry has done good service in carefully collecting and marshalling the results of the numerous researches published in various parts of the world."—*Pharmaceutical Journal.*

"At various times monographs have been printed by individual workers, but it may safely be said that Mr. Parry is the first in these latter days to deal with the subject in an adequate manner. His book is well conceived and well written. . . ."—*Chemist and Druggist.*

COSMETICS. Translated from the German of Dr. THEODOR KOLLER. Crown 8vo. 262 pp. 1902. Price 5s.; India and Colonies, 5s. 6d.; Other Countries, 6s. net.

Contents.

Preface.—Chapters I., Purposes and Uses of, and Ingredients used in the Preparation of Cosmetics.—II., Preparation of Perfumes by Pressure, Distillation, Maceration, Absorption or Enfleurage, and Extracition Methods—III., Chemical end Animal Products used in the Preparation of Cosmetics.—IV., Oils and Fats used in the Preparation of Cosmetics.—V., General Cosmetic Preparations.—VI., Mouth Washes and Tooth Pastes.—VII., Hair Dyes, Hair Restorers and Depilatories.—VIII., Cosmetic Adjuncts and Specialities—Colouring Cosmetic Preparations.—IX., Antiseptic Washes and Soaps—Toilet and Hygienic Soaps.—X., Secret Preparations for Skin, Complexion, Teeth, Mouth, etc.—XI., Testing and Examining the Materials Employed in the Manufacture of Cosmetics.—Index.

INK MANUFACTURE: Including Writing, Copying, Lithographic, Marking, Stamping, and Laundry Inks. By SIGMUND LEHNER. Three Illustrations. Crown 8vo. 162 pp. 1902. Translated from the German of the Fifth Edition. Price 5s.; India and Colonies, 5s. 6d.; Other Countries, 6s. net.

Contents.

Chapters I., Introduction.—II., Varieties of Ink.—III., Writing Inks.—IV., Raw Materials of Tannin Inks.—V., The Chemical Constitution of the Tannin Inks.—VI., Recipes for Tannin Inks.—VII., Logwood Tannin Inks.—VIII., Ferric Inks.—IX., Alizarine Inks.—X., Extract Inks.—XI., Logwood Inks.—XII., Copying Inks.—XIII., Hektographs.—XIV., Hektograph Inks.—XV., Safety Inks.—XVI., Ink Extracts and Powders.—XVII., Preserving Inks.—XVIII., Changes in Ink and the Restoration of Faded Writing.—XIX., Coloured Inks.—XX., Red Inks.—XXI., Blue Inks.—XXII., Violet Inks.—XXIII., Yellow Inks.—XXIV., Green Inks.—XXV., Metallic Inks.—XXVI., Indian Ink.—XXVII., Lithographic Inks and Pencils.—XXVIII., Ink Pencils.—XXIX., Marking Inks.—XXX., Ink Specialities.—XXXI., Sympathetic Inks.—XXXII., Stamping Inks.—XXXIII., Laundry or Washing Blue.—Index.

DRYING OILS, BOILED OIL AND SOLID AND LIQUID DRIERS. By L. E. ANDÉS. A Practical Work for Manufacturers of Oils, Varnishes, Printing Inks, Oilcloth and Linoleum, Oilcakes, Paints, etc. Expressly Written for this Series of Special Technical Books, and the Publishers hold the Copyright for English and Foreign Editions. Forty-two Illustrations. 342 pp. 1901. Demy 8vo. Price 12s. 6d.; India and Colonies, 13s. 6d.; Other Countries, 15s.; strictly net.

Contents.

Chapters I., General Chemical and Physical Properties of the Drying Oils; Cause of the Drying Property; Absorption of Oxygen; Behaviour towards Metallic Oxides, etc.—II., The Properties of and Methods for obtaining the Drying Oils.—III., Production of the Drying Oils by Expression and Extraction; Refining and Bleaching; Oil Cakes and Meal; The Refining and Bleaching of the Drying Oils; The Bleaching of Linseed Oil.—IV., The Manufacture of Boiled Oil; The Preparation of Drying Oils for Use in the Grinding of Paints and Artists' Colours and in the Manufacture of Varnishes by Heating over a Fire or by Steam, by the Cold Process, by the Action of Air, and by Means of the Electric Current; The Driers used in Boiling Linseed Oil; The Manufacture of Boiled Oil and the Apparatus therefor; Livache's Process for Preparing a Good Drying Oil and its Practical Application.—V., The Preparation of Varnishes for Letterpress, Lithographic and Copperplate Printing, for Oilcloth and Waterproof Fabrics; The Manufacture of Thickened Linseed Oil, Burnt Oil, Stand Oil by Fire Heat, Superheated Steam, and by a Current of Air.—VI., Behaviour of the Drying Oils and Boiled Oils towards Atmospheric Influences, Water, Acids and Alkalies.—VII., Boiled Oil Substitutes.—VIII., The Manufacture of Solid and Liquid Driers from Linseed Oil and Rosin; Linolic Acid Compounds of the Driers.—IX., The Adulteration and Examination of the Drying Oils and Boiled Oil.

REISSUE OF **CHEMICAL ESSAYS OF C. W. SCHEELE.** First Published in English in 1786. Translated from the Academy of Sciences at Stockholm, with Additions. 300 pp. Demy 8vo. 1901. Price 5s.; India and Colonies, 5s. 6d.; Other Countries, 6s.; strictly net.

Contents.

Memoir: C. W. Scheele and his work (written for this edition).—Chapters I., On Fluor Mineral and its Acid.—II., On Fluor Mineral.—III., Chemical Investigation of Fluor Acid, with a View to the Earth which it Yields, by Mr. Wiegler.—IV., Additional Information Concerning Fluor Minerals.—V., On Manganese, Magnesium, or Magnesia Vitrariorum.—VI., On Arsenic and its Acid.—VII., Remarks upon Salts of Benzoin.—VIII., On Silex, Clay and Alum.—IX., Analysis of the Calculus Vesical.—X., Method of Preparing Mercurius Dulcis Via Humida.—XI., Cheaper and more Convenient Method of Preparing Pulvis Algarothi.—XII., Experiments upon Molybdæna.—XIII., Experiments on Plumbago.—XIV., Method of Preparing a New Green Colour.—XV., Of the Decomposition of Neutral Salts by Unslaked Lime and Iron.—XVI., On the Quantity of Pure Air which is Daily Present in our Atmosphere.—XVII., On Milk and its Acid.—XVIII., On the Acid of Saccharum Lactis.—XIX., On the Constituent Parts of Lapis Ponderosus or Tungsten.—XX., Experiments and Observations on Ether.—Index.

Press Opinions.

"We would recommend the book as a refreshing recreation to the hard-worked student or investigator of the present day."—*Chemical News.*

"The present reissue renders accessible a very complete record of the researches of the great chemist."—*Chemical Trade Journal.*

"Written in a manner that cannot fail to entertain even those whose knowledge of chemical lore is of a very elementary character."—*Widnes Weekly News.*

GLUE AND GLUE TESTING. By SAMUEL RIDEAL, D.Sc. Lond., F.I.C. Fourteen Engravings. 144 pp. Demy 8vo. 1900. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net.

Contents.

Chapters I., **Constitution and Properties:** Definitions and Sources, Gelatine, Chondrin and Allied Bodies, Physical and Chemical Properties, Classification, Grades and Commercial Varieties.—II., **Raw Materials and Manufacture:** Glue Stock, Lining, Extraction, Washing and Clarifying, Filter Presses, Water Supply, Use of Alkalies, Action of Bacteria and of Antiseptics, Various Processes, Cleansing, Forming, Drying, Crushing, etc., Secondary Products.—III., **Uses of Glue:** Selection and Preparation for Use, Carpentry, Veneering, Paper-Making, Bookbinding, Printing Rollers, Hectographs, Match Manufacture, Sandpaper, etc., Substitutes for other Materials, Artificial Leather and Caoutchouc.—IV., **Gelatine:** General Characters, Liquid Gelatine. Photographic Uses, Size, Tanno-, Chrome and Formo-Gelatine, Artificial Silk, Cements, Pneumatic Tyres, Culinary, Meat Extracts, Isinglass, Medicinal and other Uses, Bacteriology.—V., **Glue Testing:** Review of Processes, Chemical Examination, Adulteration, Physical Tests, Valuation of Raw Materials.—VI., **Commercial Aspects.**

Press Opinions.

"This work is of the highest technical character."—*Carpenter and Builder.*

"Dr. Rideal's book must be regarded as a valuable contribution to other technical literature, which manufacturers, merchants and users may study with profit."—*British Trade Journal.*

TECHNOLOGY OF PETROLEUM: Oil Fields of the World—Their History, Geography and Geology—Annual Production and Development—Oil-well Drilling—Transport. By HENRY NEUBERGER and HENRY NOALHAT. Translated from the French by J. G. McINTOSH. 550 pp. 153 Illustrations. 26 Plates. Super Royal 8vo. 1901. Price 21s.; India and Colonies, 22s.; Other Countries, 23s. 6d.; strictly net.

Contents.

Part I., **Study of the Petroliferous Strata**—Chapters I., Petroleum—Definition.—II., The Genesis or Origin of Petroleum.—III., The Oil Fields of Galicia, their History.—IV., Physical Geography and Geology of the Galician Oil Fields.—V., Practical Notes on Galician Land Law—Economic Hints on Working, etc.—VI., Roumania—History, Geography, Geology.—VII., Petroleum in Russia—History.—VIII., Russian Petroleum (*continued*)—Geography and Geology of the Caucasian Oil Fields.—IX., Russian Petroleum (*continued*).—X., The Secondary Oil Fields of Europe, Northern Germany, Alsace, Italy, etc.—XI., Petroleum in France.—XII., Petroleum in Asia—Transcaspian and Turkestan Territory—Turkestan—Persia—British India and Burmah—British Burmah or Lower Burmah—China—Chinese Thibet—Japan, Formosa and Saghalien.—XIII., Petroleum in Oceania—Sumatra, Java, Borneo—Isle of Timor—Philippine Isles—New Zealand.—XIV., The United States of America—History.—XV., Physical Geology and Geography of the United States Oil Fields.—XVI., Canadian and other North American Oil Fields.—XVII., Economic Data of Work in North America.—XVIII., Petroleum in the West Indies and South America.—XIX., Petroleum in the French Colonies.

Part II., **Excavations.**—Chapter XX., Hand Excavation or Hand Digging of Oil Wells.

Part III., **Methods of Boring.**—Chapters XXI., Methods of Oil-well Drilling or Boring.—XXII., Boring Oil Wells with the Rope.—XXIII., Drilling with Rigid Rods and a Free-fall—Fabian System.—XXIV., Free-fall Drilling by Steam Power.—XXV., Oil-well Drilling by the Canadian System.—XXVI., Drilling Oil Wells on the Combined System.—XXVII., Comparison between the Combined Fauck System and the Canadian.—XXVIII., The American System of Drilling with the Rope.—XXIX., Hydraulic Boring with the Drill by Hand and Steam Power.—XXX., Rotary Drilling of Oil Wells, Bits, Steel-crowned Tools, Diamond Tools—Hand Power and Steam Power—Hydraulic Sand-pumping.—XXXI., Improvements in and different Systems of Drilling Oil Wells.

Part IV., **Accidents.**—Chapters XXXII., Boring Accidents—Methods of preventing them—Methods of remedying them.—XXXIII., Explosives and the use of the "Torpedo" Levigation.—XXXIV., Storing and Transport of Petroleum.—XXXV., General Advice—Prospecting, Management and carrying on of Petroleum Boring Operations.

Part V., **General Data.—Customary Formulæ.**—Memento. Practical Part. General Data bearing on Petroleum.—Glossary of Technical Terms used in the Petroleum Industry.—Copious Index.

Press Opinions.

"The book is undoubtedly one of the most valuable treatises that can be placed in the hands of all who desire a knowledge of petroleum."—*Liverpool Journal of Commerce.*

"The book will undoubtedly take a high place in the literature of petroleum."—*Liverpool Post.*

"We should like to say that the translator has accomplished his difficult task, so full of technical difficulties, with a great amount of success."—*Petroleum.*

A DICTIONARY OF CHEMICALS AND RAW PRODUCTS USED IN THE MANUFACTURE OF PAINTS, COLOURS, VARNISHES AND ALLIED PREPARATIONS. By George H. Hurst, F.C.S. Demy 8vo. 380 pp. 1901. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

The names of the Chemicals and Raw Products are arranged in alphabetical order, and the description of each varies in length from half to eight pages. The following are some of the articles described and explained: Acetates—Acetic Acid—Acidimetry—Alcohol—Alum—Ammonia—Amber—Animi—Arsenic—Beeswax—Benzol—Bichromates of Potash and Soda—Bleaching Powder—Bone Black—Boric Acid—Brunswick Green—Cadmium Yellow—Carbonates—Carmine—Carnauba Wax—Caustic Potash and Soda—Chrome Colours—Clay—Coal Tar Colours—Copal—Dammar—Drying Oils—Emerald Green—Gamboge—Glue—Glycerine—Gums—Gypsum—Indian Red—Japanese Lacquer—Lac—Lakes—Lamp Black—Lead Compounds—Linseed Oil—Magnesia—Manganese Compounds—Mica—Nitric Acid—Ochres—Orange Lead—Orr's White—Paraffin—Prussian Blue—Rosin Oil—Sepia—Sienna—Smalts—Sodium Carbonate—Sublimed White Lead—Sulphuric Acid—Terra Verte—Testing Pigments—Turpentine—Ultramarine—Umbers—Vermilionettes—White Lead—Whiting—Zinc Compounds.—Appendix: Comparison of Baumé Hydrometer and Specific Gravity for Liquids Lighter than Water—Hydrometer Table for Liquids Heavier than Water—Comparison of Temperature Degrees—Tables for Converting French Metric Weights and Measures into English—Table of the Elements—etc., etc.—Copious Index.

Press Opinions.

"This treatise will be welcomed by those interested in this industry who have not secured the full advantage of a course of scientific training."—*Chemical Trade Journal.*

"In concise and lucid terms almost every ingredient used in paint and colour manufacture is described together with the methods of testing their intrinsic and chemical value."—*Pontefract Express.*

"Such a book of reference for paint, colour and varnish manufacturers has long been needed."—*Manchester Courier.*

RECIPES FOR THE COLOUR, PAINT, VARNISH, OIL, SOAP AND DRYSALTERY TRADES. Compiled by AN ANALYTICAL CHEMIST. 350 pp. 1902. Demy 8vo. Price 7s. 6d; India and British Colonies, 8s.; Other Countries, 8s. 6d; strictly net.

Contents.

Compiler's Preface. — Sections I., Pigments or Colours for Paints, Lithographic and Letterpress Printing Inks, etc.—II., Mixed Paints and Preparations for Paint-making, Painting, Lime-washing, Paperhanging, etc.—III., Varnishes for Coach-builders, Cabinet-makers, Wood-workers, Metal-workers, Photographers, etc.—IV., Soaps for Toilet, Cleansing, Polishing, etc.—V., Perfumes.—VI., Lubricating Greases, Oils, etc.—VII., Cements, Pastes, Glues and Other Adhesive Preparations.—VIII., Writing, Marking, Endorsing and Other Inks —Sealing-wax and Office Requisites.—IX. Preparations for the Laundry, Kitchen, Stable and General Household Uses.—X., Disinfectant Preparations.—XI. Miscellaneous Preparations.—Index.

PURE AIR, OZONE AND WATER. A Practical Treatise of their Utilisation and Value in Oil, Grease, Soap, Paint, Glue and other Industries. By W. B. COWELL. Twelve Illustrations. Crown 8vo. 85 pp. 1900. Price 5s.; India and Colonies, 5s. 6d.; Other Countries, 6s.; strictly net.

Contents.

Chapters I., Atmospheric Air; Lifting of Liquids; Suction Process; Preparing Blown Oils; Preparing Siccative Drying Oils.—II., Compressed Air; Whitewash.—III., Liquid Air; Retrocession.—IV., Purification of Water; Water Hardness.—V., Fleshings and Bones.—VI., Ozonised Air in the Bleaching and Deodorising of Fats, Glues, etc.; Bleaching Textile Fibres.—Appendix: Air and Gases; Pressure of Air at Various Temperatures; Fuel; Table of Combustibles; Saving of Fuel by Heating Feed Water; Table of Solubilities of Scale Making Minerals; British Thermal Units Tables; Volume of the Flow of Steam into the Atmosphere; Temperature of Steam.—Index.

THE MANUFACTURE OF MINERAL AND LAKE PIGMENTS. Containing Directions for the Manufacture of all Artificial, Artists and Painters' Colours, Enamel, Soot and Metallic Pigments. A Text-book for Manufacturers, Merchants, Artists and Painters. By Dr. JOSEF BERSCH. Translated from the Second Revised Edition by ARTHUR C. WRIGHT, M.A. (Oxon.), B.Sc. (Lond.), formerly Assistant Lecturer and Demonstrator in Chemistry at the Yorkshire College, Leeds. Forty-three Illustrations. 476 pp., demy 8vo. 1901. Price 12s. 6d.; India and Colonies, 13s. 6d.; Other Countries, 15s.; strictly net.

Contents.

Chapters I., Introduction.—II., Physico-chemical Behaviour of Pigments.—III., Raw Materials Employed in the Manufacture of Pigments.—IV., Assistant Materials.—V., Metallic Compounds.—VI., The Manufacture of Mineral Pigments.—VII., The Manufacture of White Lead.—VIII., Enamel White.—IX., Washing Apparatus.—X., Zinc White.—XI., Yellow Mineral Pigments.—XII., Chrome Yellow.—XIII., Lead Oxide Pigments.—XIV., Other Yellow Pigments.—XV., Mosaic Gold.—XVI., Red Mineral Pigments.—XVII., The Manufacture of Vermilion.—XVIII., Antimony Vermilion.—XIX., Ferric Oxide Pigments.—XX., Other Red Mineral Pigments.—XXI., Purple of Cassius.—XXII., Blue Mineral Pigments.—XXIII., Ultramarine.—XXIV., Manufacture of Ultramarine.—XXV., Blue Copper Pigments.—XXVI., Blue Cobalt Pigments.—XXVII., Smalts.—XXVIII., Green Mineral Pigments.—XXIX., Emerald Green.—XXX., Verdigris.—XXXI., Chromium Oxide.—XXXII., Other Green Chromium Pigments.—XXXIII., Green Cobalt Pigments.—XXXIV., Green Manganese Pigments.—XXXV., Compounded Green Pigments.—XXXVI., Violet Mineral Pigments.—XXXVII., Brown Mineral Pigments.—XXXVIII., Brown Decomposition Products.—XXXIX., Black Pigments.—XL., Manufacture of Soot Pigments.—XLI., Manufacture of Lamp Black.—XLII., The Manufacture of Soot Black without Chambers.—XLIII., Indian Ink.—XLIV., Enamel Colours.—XLV., Metallic Pigments.—XLVI., Bronze Pigments—XLVII., Vegetable Bronze Pigments.

PIGMENTS OF ORGANIC ORIGIN.—Chapters XLVIII., Lakes.—XLIX., Yellow Lakes.—L., Red Lakes.—LI., Manufacture of Carmine.—LII., The Colouring Matter of Lac.—LIII., Saffower or Carthamine Red.—LIV., Madder and its Colouring Matters.—LV., Madder Lakes.—LVI., Manjit (Indian Madder).—LVII., Lichen Colouring Matters.—LVIII., Red Wood Lakes.—LIX., The Colouring Matters of Sandal Wood and Other Dye Woods.—LX., Blue Lakes.—LXI., Indigo Carmine.—LXII., The Colouring Matter of Log Wood.—LXIII., Green Lakes.—LXIV., Brown Organic Pigments.—LXV., Sap Colours.—LXVI., Water Colours.—LXVII., Crayons.—LXVIII., Confectionery Colours.—LXIX., The Preparation of Pigments for Painting.—LXX., The Examination of Pigments.—LXXI., Examination of Lakes.—LXXII., The Testing of Dye-Woods.—LXXIII., The Design of a Colour Works.—LXXIV.—Commercial Names of Pigments.—Appendix: Conversion of Metric to English Weights and Measures.—Centigrade and Fahrenheit Thermometer Scales.—Index.

BONE PRODUCTS AND MANURES: An Account of the most recent Improvements in the Manufacture of Fat, Glue, Animal Charcoal, Size, Gelatine and Manures. By THOMAS LAMBERT, Technical and Consulting Chemist. Illustrated by Twenty-one Plans and Diagrams. 162 pp., demy 8vo. 1901. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., Chemical Composition of Bones—Arrangement of Factory—Crushing of Bones—Treatment with Benzene—Benzene in Crude Fat—Analyses of Clarified Fats—Mechanical Cleansing of Bones—Animal Charcoal—Tar and Ammoniacal Liquor, Char and Gases, from good quality Bones—Method of Retorting the Bones—Analyses of Chars—"Spent" Chars—Cooling of Tar and Ammoniacal Vapours—Value of Nitrogen for Cyanide of Potash—Bone Oil—Marrow Bones—Composition of Marrow Fat—Premier Juice—Buttons.—II., Properties of Glue—Glutin and Chondrin—Skin Glue—Liming of Skins—Washing—Boiling of Skins—Clarification of Glue Liquors—Acid Steeping of Bones—Water System of Boiling Bones—Steam Method of Treating Bones—Nitrogen in the Treated Bones—Glue-Boiling and Clarifying-House—Plan showing Arrangement of Clarifying Vats—Plan showing Position of Evaporators—Description of Evaporators—Sulphurous Acid Generator—Clarification of Liquors—Section of Drying-House—Specification of a Glue—Size—Uses and Preparation and Composition of Size—Concentrated Size.—III., Properties of Gelatine—Preparation of Skin Gelatine—Washing—Bleaching—Boiling—Clarification—Evaporation—Drying—Bone Gelatine—Selecting Bones—Crushing—Dissolving—Bleaching—Boiling—Properties of Glutin and Chondrin—Testing of Glues and Gelatines.—IV., The Uses of Glue, Gelatine and Size in Various Trades—Soluble and Liquid Glues—Steam and Waterproof Glues.—V., Manures—Importation of Food Stuffs—Soils—Germination—Plant Life.—VI., Natural Manures—Water and Nitrogen in Farmyard Manure—Full Analysis of Farmyard Manure—Action on Crops—Water-Closet System—Sewage Manure—Green Manures.—VII., Artificial Manures—Bones—Boiled and Steamed Bones—Mineral Phosphates—English Coprolites—French and Spanish Phosphorites—German and Belgian Phosphates—Basic Slag—Guanos Proper—Guano Phosphates.—VIII., Mineral Manures—Common Salt—Potash Salts—Calcareous Manures—Prepared Nitrogenous Manures—Ammoniacal Compounds—Sodium Nitrate—Potassium Nitrate—Organic Nitrogenous Matters—Shoddy—Hoofs and Horns—Leather Waste—Dried Meat—Dried Blood—Superphosphates—Composition—Manufactu e—Section of Manure-Shed—First and Ground Floor Plans of Manure-Shed—Quality of Acid Used—Mixings—Special Manures—Potato Manure—Dissolved Bones—Dissolved Bone Compound—Enriched Peruvian Guano—Special Manure for Garden Stuffs, etc.—Special Manure for Grass Lands—Special Tobacco Manures—Sugar-Cane Manure—Compounding of Manures—Valuation of Manures.—IX., Analyses of Raw and Finished Products—Common Raw Bones—Degreased Bones—Crude Fat—Refined Fat—Degelatinised Bones—Animal Charcoal—Bone Superphosphates—Guanos—Dried Animal Products—Potash Compounds—Sulphate of Ammonia—Extraction in Vacuo—Description of a Vacuum Pan—French and British Gelatines compared.—Index.

Press Opinion.

"We can with confidence recommend the perusal of the book to all persons interested in the manufacture of artificial manures, and also to the large number of farmers and others who are desirous of working their holdings on the most up-to-date methods, and obtaining the best possible results, which scientific research has placed within their reach."—*Wigan Observer.*

ANALYSIS OF RESINS AND BALSAMS. Translated from the German of Dr. KARL DIETERICH. Demy 8vo. 340 pp. 1901. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Part I., Definition of Resins in General—Definition of Balsams, and especially the Gum Resins—External and Superficial Characteristics of Resinous Bodies—Distinction between Resinous Bodies and Fats and Oils—Origin, Occurrence and Collection of Resinous Substances—Classification—Chemical Constituents of Resinous Substances—Resinols—Resinot Annols—Behaviour of Resin Constituents towards the Cholesterine Reactions—Uses and Identification of Resins—Melting-point—Solvents—Acid Value—Saponification Value—Resin Value—Ester and Ether Values—Acetyl and Corbonyl Value—Methyl Value—Resin Acid—Systematic Résumé of the Performance of the Acid and Saponification Value Tests.

Part II., Balsams—Introduction—Definitions—Canada Balsam—Copaiba Balsam—Angostura Copaiba Balsam—Bahia Copaiba Balsam—Carthagena Copaiba Balsam—Maracaibo Copaiba Balsam—Maturin Copaiba Balsam—Gurjum Copaiba Balsam—Para Copaiba Balsam—Surinam Copaiba Balsam—West African Copaiba Balsam—Mecca Balsam—Peruvian Balsam—Tolu Balsam—Acaroid Resin—Amine—Amber—African and West Indian Kino—Bengal Kino—Labdanum—Mastic—Pine Resin—Sandarach—Scammonium—Shellac—Storax—Adulteration of Styrax Liquidus Crudus—Purified Storax—Styrax Crudus Colatus—Tacamahac—Thapsia Resin—Turpentine—Chios Turpentine—Strassburg Turpentine—Turpeth Turpentine. **Gum Resins**—Ammoniacum—Bdellium—Euphorbium—Galbanum—Gamboge—Lactucarium—Myrrh—Opopanax—Sagapenum—Olibanum or Incense—Acaroid Resin—Amber—Thapsia Resin.—Index.

MANUFACTURE OF PAINT. A Practical Handbook for Paint Manufacturers, Merchants and Painters. By J. CRUICKSHANK SMITH, B.Sc. Demy 8vo. 1901. 200 pp. Sixty Illustrations and One Large Diagram. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Part I., Chapters I., Preparation of Raw Material.—II., Storing of Raw Material.—III., Testing and Valuation of Raw Material—Paint Plant and Machinery.

Part II., Chapters V., The Grinding of White Lead.—VI., Grinding of White Zinc.—VII., Grinding of other White Pigments.—VIII., Grinding of Oxide Paints.—IX., Grinding of Staining Colours.—X., Grinding of Black Paints.—XI., Grinding of Chemical Colours—Yellows.—XII., Grinding of Chemical Colours—Blues.—XIII., Grinding Greens.—XIV., Grinding Reds.—XV., Grinding Lakes.—XVI., Grinding Colours in Water.—XVII., Grinding Colours in Turpentine.

Part III., Chapters XVIII., The Uses of Paint.—XIX., Testing and Matching Paints.—XX., Economic Considerations.—Index.

Press Opinions.

"Will fill a place hitherto unoccupied: . . . bears all the marks of thoroughness both on the scientific and technical side. That it will take its place as the standard book of its subject may safely be predicted."—*Aberdeen Free Press.*

"This is a workmanlike manual of the methods and processes of an industry known to the world at large only by its remote results. . . . This clearly written and well-informed handbook gives a plain exposition of these matters, and cannot but prove useful to manufacturers and merchants, and to painters curious about the materials in which they work."—*The Scotsman.*

"Mr. Smith's book is practical throughout, and it will be found helpful to those engaged in the industry and those who make use of paints."—*The Architect.*

"It is an important text-book for students attending technical classes in these subjects, concisely setting forth in a most practical manner many intricate details in the preparation and production of paint during the operation of grinding. . . . The work should occupy a position on the bookshelf of every individual interested in paint."—*The Decorators' and Painters' Magazine.*

THE CHEMISTRY OF PIGMENTS. By ERNEST J. PARRY, B.Sc. (Lond.), F.I.C., F.C.S., and J. H. COSTE, F.I.C., F.C.S. Demy 8vo. Five Illustrations. 285 pp. 1902. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net.

Contents.

Chapter I., **Introductory.** Light—White Light—The Spectrum—The Invisible Spectrum—Normal Spectrum—Simple Nature of Pure Spectral Colour—The Recomposition of White Light—Primary and Complementary Colours—Coloured Bodies—Absorption Spectra.—Chapter II., **The Application of Pigments.** Uses of Pigments: Artistic, Decorative, Protective—Methods of Application of Pigments: Pastels and Crayons, Water Colour, Tempera Painting, Fresco, Encaustic Painting, Oil-colour Painting, Keramic Art, Enamel, Stained and Painted Glass, Mosaic.—Chapter III., **Inorganic Pigments.** White Lead—Zinc White—Enamel White—Whitening—Red Lead—Litharge—Vermilion—Royal Scarlet—The Chromium Greens—Chromates of Lead, Zinc, Silver and Mercury—Brunswick Green—The Ochres—Indian Red—Venetian Red—Siennas and Umbers—Light Red—Cappagh Brown—Red Oxides—Mars Colours—Terre Verte—Prussian Brown—Cobalt Colours—Cœruleum—Smalt—Copper Pigments—Malachite—Bremen Green—Scheele's Green—Emerald Green—Verdigris—Brunswick Green—Non-arsenical Greens—Copper Blues—Ultramarine—Carbon Pigments—Ivory Black—Lamp Black—Bistre—Naples Yellow—Arsenic Sulphides: Orpiment, Realgar—Cadmium Yellow—Vandyck Brown.—Chapter IV., **Organic Pigments.** Prussian Blue—Natural Lakes—Cochineal—Carmine—Crimson—Lac Dye—Scarlet—Madder—Alizarin—Campeachy—Quercitron—Rhamnus—Brazil Wood—Alkanet—Santal Wood—Archil—Coal-tar Lakes—Red Lakes—Alizarin Compounds—Orange and Yellow Lakes—Green and Blue Lakes—Indigo—Dragon's Blood—Gamboge—Sepia—Indian Yellow, Puree—Bitumen, Asphaltum, Mummy.—**Index.**

LEAD AND ITS COMPOUNDS. By THOS. LAMBERT, Technical and Consulting Chemist. Demy 8vo. 200 pp. Forty Illustrations. 1902. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d. net. Plans and Diagrams.

Contents.

Chapters I., History—Ores of Lead.—II., Geographical Distribution of the Lead Industry.—III., Chemical and Physical Properties of Lead—Alloys of Lead—Compounds of Lead.—IV., Dressing of Lead Ores.—V., Smelting of Lead Ores—Smelting in the Scotch or American Ore-hearth—Smelting in the Shaft or Blast Furnace.—VI., Condensation of Lead Fume.—VII., Desilverisation, or the Separation of Silver from Argentiferous Lead—Cupellation.—VIII., The Manufacture of Lead Pipes and Sheets.—IX., Protoxide of Lead—Litharge and Massicot—Red Lead or Minium—X., Lead Poisoning.—XI., Lead Substitutes.—XII., Zinc and its Compounds.—XIII., Pumice Stone.—XIV., Drying Oils and Siccatives.—XV., Oil of Turpentine Resin.—XVI., Classification of Mineral Pigments.—XVII., Analysis of Raw and Finished Products.—Tables.—Index

NOTES ON LEAD ORES: Their Distribution and Properties. By JAS. FAIRIE, F.G.S. Crown 8vo. 1901. 64 pages. Price 2s. 6d.; Abroad, 3s.; strictly net.

Contents.

Chapters I., Definitions—Properties—Occurrence.—II., Galena—Johnstonite—Cerussite—Céruse (White Lead)—Minium—Red Lead.—III., Pyromorphite—Mimetene—Hedyphane—Crocoise—Wulfenite.—Vanadinite—IV., Bleiglätte—Anglesite—Caledonite—Linarite—Lanarkite—Leadhillite — Susannite— Clausthalite — Cotunnite.—V., Mendipite — Matlockite — Cromfordite—Nagyagite—Altaite—Melanochroite — Vauguelinite — Scheeletine.—VI., Plattnerite—Tilkerodite—Raphanosmite—Deckenite—Descloezite—Dufrenaysite — Bleinierite — Moffrasite —Geocronite — Kilbrechenite — Schulzite—Boulangerite — Heteromorphite — Meneghinite—Jamesonite — Plagionite — Zinkenite.—VII., Kobellite — Bournonite— Selenkupferblei—Nussierite—Percylite—Wolchite—Polysphacrite—Miesite.—Index.

THE RISKS AND DANGERS OF VARIOUS OCCUPATIONS AND THEIR PREVENTION. By LEONARD A. PARRY, M.D., B.S. (Lond.). 196 pp. Demy 8vo. 1900. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., Occupations which are Accompanied by the Generation and Scattering of Abnormal Quantities of Dust.—II., Trades in which there is Danger of Metallic Poisoning.—III., Certain Chemical Trades.—IV., Some Miscellaneous Occupations.—V., Trades in which Various Poisonous Vapours are Inhaled.—VI., General Hygienic Considerations.—Index.

PRACTICAL X RAY WORK. By FRANK T. ADDYMAN, B.Sc. (Lond.), F.I.C., Member of the Roentgen Society of London; Radiographer to St. George's Hospital; Demonstrator of Physics and Chemistry, and Teacher of Radiography in St. George's Hospital Medical School. Demy 8vo. Twelve Plates from Photographs of X Ray Work. Fifty-two Illustrations. 200 pp. 1901. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net.

Contents.

Part I., **Historical**—Chapters I., Introduction.—II., Work leading up to the Discovery of the X Rays.—III., The Discovery.

Part II., **Apparatus and its Management**—Chapters I., Electrical Terms.—II., Sources of Electricity.—III., Induction Coils.—IV., Electrostatic Machines.—V., Tubes.—VI., Air Pumps.—VII., Tube Holders and Stereoscopic Apparatus.—VIII., Fluorescent Screens.

Part III., **Practical X Ray Work**—Chapters I., Installations.—II., Radioscopy.—III., Radiography.—IV., X Rays in Dentistry.—V., X Rays in Chemistry.—VI., X Rays in War.—Index.

List of Plates.

Frontispiece—Congenital Dislocation of Hip-Joint.—I., Needle in Finger.—II., Needle in Foot.—III., Revolver Bullet in Calf and Leg.—IV., A Method of Localisation.—V., Stellate Fracture of Patella showing shadow of "Strapping".—VI., Sarcoma.—VII., Six-weeks'-old Injury to Elbow showing new Growth of Bone.—VIII., Old Fracture of Tibia and Fibula badly set.—IX., Heart Shadow.—X., Fractured Femur showing Grain of Splint.—XI., Barrell's Method of Localisation.

India-Rubber and Gutta Percha.

INDIA-RUBBER AND GUTTA PERCHA. Translated from the French of T. SULIGMANN, G. LAMY, TORVILHON and H. FALCONNET. Royal 8vo. Eighty-six Illustrations. Three Plates. About 400 pages. 1902. [*In the press.*

Contents.

Part I.—Chapters I., Botanical Origin.—II., Climatology—Soil—Rational Culture and Acclimation of the Different Species of India-Rubber Plants.—III., Methods of Obtaining the Latex—Methods of Preparing Raw or Crude India-Rubber.—IV., Classification of the Commercial Species of Raw Rubber.—V., Physical and Chemical Properties of the Latex and of India-Rubber.—VI. and VII., Mechanical Transformation of Natural Caoutchouc into Washed or Normal Caoutchouc (Purification) and Normal Rubber into Masticated Rubber—Softening, Cutting, Washing, Drying—Preliminary Observations.—VIII., Vulcanisation of Normal Rubber.—IX., Chemical and Physical Properties of Vulcanised Rubber—General Considerations.—X., Hardened Rubber or Ebonite.—XI., Considerations on Mineralisation and other Mixtures—Coloration and Dyeing—Analysis of Natural or Normal Rubber and Vulcanised Rubber.—XII., Rubber Substitutes—Imitation Rubber.

Part II.—**Gutta Percha.**—Chapters I., Botanical Origin.—II., Climatology—Soil—Rational Culture.—III., Methods of Collection.—IV., Classification of the Different Species of Commercial Gutta Percha.—V., Physical and Chemical Properties.—VI., Mechanical Transformation.—VII., Methods of Analysing.—VIII., Gutta Percha Substitutes.—Index.

DRYING BY MEANS OF AIR AND STEAM. Explanations, Formulæ, and Tables for Use in Practice. Translated from the German of E. HAUSBRAND. Two folding Diagrams and Thirteen Tables. Crown 8vo. 1901. 72 pp. Price 5s.; India and Colonies, 5s. 6d.; Other Countries, 6s.; strictly net.

Contents.

Preface.—British and Metric Systems Compared—Centigrade and Fahr. Thermometers.—Chapters I., Introduction.—II., Estimation of the Maximum Weight of Saturated Aqueous Vapour which can be contained in 1 kilo. of Air at Different Pressure and Temperatures.—III., Calculation of the Necessary Weight and Volume of Air, and of the Least Expenditure of Heat, per Drying Apparatus with Heated Air, at the Atmospheric Pressure: *A*, With the Assumption that the Air is *Completely Saturated* with Vapour both before Entry and after Exit from the Apparatus.—*B*, When the Atmospheric Air is Completely Saturated *before entry*, but at its *exit* is *only* $\frac{3}{4}$, $\frac{1}{2}$ or $\frac{1}{4}$ Saturated.—*C*, When the Atmospheric Air is *not* Saturated with Moisture before Entering the Drying Apparatus.—IV., Drying Apparatus, in which, in the Drying Chamber, a Pressure is Artificially Created, Higher or Lower than that of the Atmosphere.—V., Drying by Means of Superheated Steam, without Air.—VI., Heating Surface, Velocity of the Air Current, Dimensions of the Drying Room, Surface of the Drying Material, Losses of Heat.—Index.

EVAPORATING, CONDENSING AND COOLING APPARATUS. Explanations, Formulæ and Tables for Use in Practice. By E. HAUSBRAND, Engineer. Translated from the Second Revised German Edition by A. C. WRIGHT, M.A. (Oxon.), B.Sc. (Lond.), formerly Assistant Lecturer and Demonstrator in Chemistry at the Yorkshire College, Leeds. With Twenty-one Illustrations and Seventy-six Tables. Demy 8vo. 1902. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s. net.

Contents.

Prefaces.—List of Tables.—Metric and British Systems and Thermometers compared.—Symbols and Contractions.—Introduction.—Chapters I., *Re*Coefficient of Transmission of Heat, k, and the Mean Temperature Difference, θ_m.—II., Parallel and Opposite Currents.—III., Apparatus for Heating with Direct Fire.—IV., The Injection of Saturated Steam.—V., Superheated Steam.—VI., Evaporation by Means of Hot Liquids.—VII., The Transference of Heat in General, and Transference by means of Saturated Steam in Particular.—VIII., The Transference of Heat from Saturated Steam in Pipes (Coils) and Double Bottoms.—IX., Evaporation in a Vacuum.—X., The Multiple-effect Evaporator.—XI., Multiple-effect Evaporators from which Extra Steam is Taken.—XII., The Weight of Water which must be Evaporated from 100 Kilos. of Liquor in order its Original Percentage of Dry Materials from 1-25 per cent. up to 20-70 per cent.—XIII., The Relative Proportion of the Heating Surfaces in the Elements of the Multiple Evaporator and their Actual Dimensions.—XIV., The Pressure Exerted by Currents of Steam and Gas upon Floating Drops of Water.—XV., The Motion of Floating Drops of Water upon which Press Currents of Steam.—XVI., The Splashing of Evaporating Liquids.—XVII., The Diameter of Pipes for Steam, Alcohol, Vapour and Air.—XVIII., The Diameter of Water Pipes.—XIX., The Loss of Heat from Apparatus and Pipes to the Surrounding Air, and Means for Preventing the Loss.—XX., Condensers.—XXI., Heating Liquids by Means of Steam.—XXII., The Cooling of Liquids.—XXIII., The Volumes to be Exhausted from Condensers by the Air-pumps.—XXIV., A Few Remarks on Air-pumps and the Vacua they Produce.—XXV., The Volumetric Efficiency of Air-pumps.—XXVI., The Volumes of Air which must be Exhausted from a Vessel in order to Reduce its Original Pressure to a Certain Lower Pressure.—Index.

Leather Trades.

THE LEATHER WORKER'S MANUAL. Being a Compendium of Practical Recipes and Working Formulæ for Curriers, Bootmakers, Leather Dressers, Blacking Manufacturers, Saddlers, Fancy Leather Workers, and all Persons engaged in the Manipulation of Leather. By H. C. STANDAGE. 165 pp. 1900. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., Blackings, Polishes, Glosses, Dressings, Renovators, etc., for Boot and Shoe Leather.—II., Harness Blackings, Dressings, Greases, Compositions, Soaps, and Boot-top Powders and Liquids, etc., etc.—III., Leather Grinders' Sundries.—IV., Currier's Seasonings, Blacking Compounds, Dressings, Finishes, Glosses, etc.—V., Dyes and Stains for Leather.—VI., Miscellaneous Information.—VII., Chrome Tannage.—Index.

Press Opinions.

"The book being absolutely unique."—*Birmingham Gazette.*

"This is a valuable collection of practical receipts and working formulæ for the use of those engaged in the manipulation of leather."—*Liverpool Mercury.*

PRACTICAL TREATISE ON THE LEATHER INDUSTRY. By A. M. VILLON. A Translation of Villon's "Traité Pratique de la Fabrication des cuirs et du Travail des Peaux". By FRANK T. ADDYMAN, B.Sc. (Lond.), F.I.C., F.C.S.; and Corrected by an Eminent Member of the Trade. 500 pp., royal 8vo. 1901. 123 Illustrations. Price 21s.; India and Colonies, 22s.; Other Countries, 23s. 6d.; strictly net.

Contents.

Preface—Translator's Preface—List of Illustrations.

Part I., **Materials used in Tanning**—Chapter I., Skins: I., Skin and its Structure; II., Skins used in Tanning; III., Various Skins and their Uses—Chapter II., Tannin and Tanning Substances: I., Tannin; II., Barks (Oak); III., Barks other than Oak; IV., Tanning Woods; V., Tannin-bearing Leaves; VI., Excrescences; VII., Tan-bearing Fruits; VIII., Tan-bearing Roots and Bulbs; IX., Tanning Juices; X., Tanning Substances used in Various Countries; XI., Tannin Extracts; XII., Estimation of Tannin and Tannin Principles.

Part II., **Tanning**—Chapter I., The Installation of a Tannary: I., Tan Furnaces; II., Chimneys, Boilers, etc.; III., Steam Engines—Chapter II., Grinding and Trituration of Tanning Substances: I., Cutting up Bark; II., Grinding Bark; III., The Grinding of Tan Woods; IV., Powdering Fruit, Galls and Grains; V., Notes on the Grinding of Bark—Chapter III., Manufacture of Sole Leather: I., Soaking; II., Sweating and Unhairing; III., Plumping and Colouring; IV., Handling; V., Tanning; VI., Tanning Elephants' Hides; VII., Drying; VIII., Striking or Pinning—Chapter IV., Manufacture of Dressing Leather: I., Soaking; II., Depilation; III., New Processes for the Depilation of Skins; IV., Tanning; V., Cow Hides; VI., Horse Hides; VII., Goat Skins; Manufacture of Split Hides—Chapter V., On Various Methods of Tanning: I., Mechanical Methods; II., Physical Methods; III., Chemical Methods; IV., Tanning with Extracts—Chapter VI., Quantity and Quality: I., Quantity; II., Net Cost; III., Quality of Leather—Chapter VII., Various Manipulations of Tanned Leather: I., Second Tanning; II., Grease Stains; III., Bleaching Leather; IV., Waterproofing Leather; V., Weighting Tanned Leather; VI., Preservation of Leather—Chapter VIII., Tanning Various Skins.

Part III., **Currying**—Chapter I., Waxed Calf: I., Preparation; II., Shaving; III., Stretching or Slicking; IV., Oiling the Grain; V., Oiling the Flesh Side; VI., Whitening and Graining; VII., Waxing; VIII., Finishing; IX., Dry Finishing; X., Finishing in Colour; XI., Cost—Chapter II., White Calf: I., Finishing in White—Chapter III., Cow Hide for Upper Leathers: I., Black Cow Hide; II., White Cow Hide; III., Coloured Cow Hide.—Chapter IV., Smooth Cow Hide—Chapter V., Black Leather—Chapter VI., Miscellaneous Hides: I., Horse; II., Goat; III., Waxed Goat Skin; IV., Matt Goat Skin—Chapter VII., Russia Leather: I., Russia Leather; II., Artificial Prussia Leather.

Part IV., **Enamelled, Hungary and Chamoy Leather, Morocco, Parchment, Furs and Artificial Leather**—Chapter I., Enamelled Leather: I., Varnish Manufacture; II., Application of the Enamel; III., Enamelling in Colour—Chapter II., Hungary Leather: I., Preliminary; II., Wet Work or Preparation; III., Aluming; IV., Dressing or Loft Work; V., Tallowing; VI., Hungary Leather from Various Hides—Chapter III., Tawing: I., Preparatory Operations; II., Dressing; III., Dyeing Tawed Skins; IV., Rugs—Chapter IV., Chamoy Leather—Chapter V., Morocco: I., Preliminary Operations, II., Morocco Tanning; III., Mordants used in Morocco Manufacture; IV., Natural Colours used in Morocco Dyeing; V., Artificial Colours; VI. Different Methods of Dyeing; VII., Dyeing with Natural Colours; VIII., Dyeing with Aniline Colours; IX., Dyeing with Metallic Salts; X., Leather Printing; XI., Finishing Morocco; XII., Shagreen; XIII., Bronzed Leather—Chapter VI., Gilding and Silvering: I., Gilding; II., Silvering; III., Nickel and Cobalt—Chapter VII. Parchment—Chapter VIII., Furs and Furriery: I., Preliminary Remarks; II., Indigenous Furs; III., Foreign Furs from Hot Countries; IV. Foreign Furs from Cold Countries; V., Furs from Birds' Skins; VI., Preparation of Furs; VII., Dressing; VIII., Colouring; IX., Preparation of Birds' Skins; X. Preservation of Furs—Chapter IX., Artificial Leather: I., Leather made from Scraps; II., Compressed Leather; III., American Cloth; IV., Papier Mâché; V., Linoleum; VI., Artificial Leather.

Part V., **Leather Testing and the Theory of Tanning**—Chapter I., Testing and Analysis of Leather: I., Physical Testing of Tanned Leather; II., Chemical Analysis—Chapter II., The Theory of Tanning and the other Operations of the Leather and Skin Industry: I., Theory of Soaking; II., Theory of Unhairing; III., Theory of Swelling; IV., Theory of Handling; V. Theory of Tanning; VI., Theory of the Action of Tannin on the Skin; VII., Theory of Hungary Leather Making; VIII., Theory of Tawing; IX., Theory of Chamoy Leather Making; X., Theory of Mineral Tanning.

Part VI., **Uses of Leather**—Chapter I., Machine Belts: I., Manufacture of Belting; II., Leather Chain Belts; III., Various Belts, IV., Use of Belts—Chapter II., Boot and Shoemaking: I., Boots and Shoes; II., Laces—Chapter III., Saddlery: I., Composition of a Saddle; II., Construction of a Saddle—Chapter IV., Harness: I., The Pack Saddle; II., Harness—Chapter V., Military Equipment—Chapter VI., Glove Making—Chapter VII., Carriage Building—Chapter VIII., Mechanical Uses.

Appendix, **The World's Commerce in Leather**—I., Europe; II., America; III., Asia IV., Africa; Australasia—Index.

Press Opinions.

"The book is well and lucidly written."—*Shoe Manufacturers' Monthly Journal.*

"This book cannot fail to be of great value to all engaged in the leather trades. . . . "—*Midland Free Press.*

"Gives much useful and interesting information concerning the various processes by which the skins of animals are converted into leather."—*Leeds Mercury.*

"It can thus be confidently recommended to all who are more or less practically interested in the technology of a very important subject."—*Leicester Post.*

"This is, in every respect, an altogether admirable, practical, clear and lucid treatise on the various and numerous branches of the great leather industry, of which it deals in an exhaustive, highly intelligent, workmanlike and scientific manner. . . ."—*Shoe and Leather Trader.*

"It certainly should be worth the while of English tanners to see what lessons they can learn from French practice, and French practice, we should imagine, could hardly have a better exponent than the author of this large volume."—*Western Daily Press and Bristol Times.*

". . . As a work of reference the volume will be extremely useful in the trade, and where leisure affords sufficient opportunity a careful perusal and study of it would afford ample reward."—*Kettering Guardian.*

Books on Pottery, Bricks, Tiles, Glass, etc.

THE MANUAL OF PRACTICAL POTTING. Revised and Enlarged. Third Edition. 200 pp. 1901. Price 17s. 6d.; India and Colonies, 18s. 6d.; Other Countries, 20s.; strictly net.

Contents.

Introduction. The Rise and Progress of the Potter's Art.—Chapters I., **Bodies.** China and Porcelain Bodies, Parian Bodies, Semi-porcelain and Vitreous Bodies, Mortar Bodies, Earthenwares Granite and C.C. Bodies, Miscellaneous Bodies, Sagger and Crucible Clays, Coloured Bodies, Jasper Bodies, Coloured Bodies for Mosaic Painting, Encaustic Tile Bodies, Body Stains, Coloured Dips.—II., **Glazes.** China Glazes, Ironstone Glazes, Earthenware Glazes, Glazes without Lead, Miscellaneous Glazes, Coloured Glazes, Majolica Colours.—III., **Gold and Cold Colours.** Gold, Purple of Cassius, Marone and Ruby, Enamel Coloured Bases, Enamel Colour Fluxes, Enamel Colours, Mixed Enamel Colours, Antique and Vellum Enamel Colours, Underglaze Colours, Underglaze Colour Fluxes, Mixed Underglaze Colours, Flow Powders, Oils and Varnishes.—IV., **Means and Methods.** Reclamation of Waste Gold, The Use of Cobalt, Notes on Enamel Colours, Liquid or Bright Gold.—V., **Classification and Analysis.** Classification of Clay Ware, Lord Playfair's Analysis of Clays, The Markets of the World, Time and Scale of Firing, Weights of Potter's Material, Decorated Goods Count.—VI., Comparative Loss of Weight of Clays.—VII., Ground Felspar Calculations.—VIII., The Conversion of Slop Body Recipes into Dry Weight.—IX., The Cost of Prepared Earthenware Clay.—X., **Forms and Tables.** Articles of Apprenticeship, Manufacturer's Guide to Stocktaking, Table of Relative Values of Potter's Materials, Hourly Wages Table, Workman's Settling Table, Comparative Guide for Earthenware and China Manufacturers in the use of Slop Flint and Slop Stone, Foreign Terms applied to Earthenware and China Goods, Table for the Conversion of Metrical Weights and Measures on the Continent of South America.—**Index.**

CERAMIC TECHNOLOGY: Being some Aspects of Technical Science as Applied to Pottery Manufacture. Edited by CHARLES F. BINNS. 100 pp. Demy 8vo. 1897. Price 12s. 6d.; India and Colonies, 13s. 6d.; Other Countries, 15s.; strictly net.

Contents.

Preface.—Introduction.—Chapters I., The Chemistry of Pottery.—II., Analysis and Synthesis.—III., Clays and their Components.—IV., The Biscuit Oven.—V., Pyrometry.—VI., Glazes and their Composition.—VII., Colours and Colour-making.—Index.

RECIPES FOR FLINT GLASS MAKING. By a British Glass Master and Mixer. Sixty Recipes. Being Leaves from the Mixing Book of several experts in the Flint Glass Trade, containing up-to-date recipes and valuable information as to Crystal, Demi-crystal and Coloured Glass in its many varieties. It contains the recipes for cheap metal suited to pressing, blowing, etc., as well as the most costly crystal and ruby. British manufacturers have kept up the quality of this glass from the arrivals of the Venetians to Hungry Hill, Stourbridge, up to the present time. The book also contains remarks as to the result of the metal as it left the pots by the respective metal mixers, taken from their own memoranda upon the originals. 1900. Price for United Kingdom, 10s. 6d.; Abroad. 15s.; United States, $4; strictly net.

Contents.

Ruby—Ruby from Copper—Flint for using with the Ruby for Coating—A German Metal—Cornelian, or Alabaster—Sapphire Blue—Crysophis—Opal—Turquoise Blue—Gold Colour—Dark Green—Green (common)—Green for Malachite—Blue for Malachite—Black for Melachite—Black—Common Canary Batch—Canary—White Opaque Glass—Sealing-wax Red—Flint—Flint Glass (Crystal and Demi)—Achromatic Glass—Paste Glass—White Enamel—Firestone—Dead White (for moons)—White Agate—Canary—Canary Enamel—Index.

COLOURING AND DECORATION OF CERAMIC WARE. By ALEX. BRONGNIART. With Notes and Additions by ALPHONSE SALVETAT. Translated from the French. 200 pp. 1898. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

The Pastes, Bodies or Ceramic Articles Capable of being Decorated by Vitrifiable Colours—The Chemical Preparation of Vitrifiable Colours—Composition and Preparation of Vitrifiable Colours—The Oxides—Preparation of Oxides—Preparation of Chromates—Preparation of other Colours—Composition and Preparation of Fluxes—Muffle Colours—Recipes for Colours—Use of Metals—Lustres—Preparation and Application of Colours—Composition of Coloured Pastes—Underglaze Colours—Colours in the Glaze—Overglaze Colours—Painting in Vitrifiable Colours—Gilding—Burnishing—Printing—Enlarging and Reducing Gelatine Prints—Muffle Kilns for Vitrifiable Colours—Influence of the Material on the Colour—Changes Resulting from the Actions of the Fire—Alterations Resulting from the Colours—Alterations in Firing.

HOW TO ANALYSE CLAY. Practical Methods for Practical Men. By HOLDEN M. ASHBY, Professor of Organic Chemistry, Harvey Medical College, U.S.A. Twenty Illustrations. 1898. Price 2s. 6d.; Abroad, 3s.; strictly net.

Contents.

List of Apparatus—List of Atomic Weights—Use of Balance, and Burette, Sand Bath, and Water Bath—Dessicator—Drying Oven—Filtering—Fusion—Determination of Water, Organic Matter, Iron, Calcium, Alkalies, Limestone, Silica, Alumina, Magnesium, etc.—Mechanical Analysis—Rational Analysis—Standard Solutions—Volumetric Analysis—Standards for Clay Analysis—Sampling.

ARCHITECTURAL POTTERY. Bricks, Tiles, Pipes, Enamelled Terra-cottas, Ordinary and Incrusted Quarries, Stoneware Mosaics, Faïences and Architectural Stoneware. By LEON LEFÈVRE. With Five Plates. 950 Illustrations in the Text, and numerous estimates. 500 pp., royal 8vo. 1900. Translated from the French by K. H. BIRD, M.A., and W. MOORE BINNS. Price 15s.; India and Colonies, 16s.; Other Countries, 17s. 6d.; strictly net.

Contents.

Part I. **Plain Undecorated Pottery.**—Chapter I., Clays: § 1, Classification, General Geological Remarks.—Classification, Origin, Locality; § 2, General Properties and Composition: Physical Properties, Contraction, Analysis, Influence of Various Substances on the Properties of Clays; § 3, Working of Clay-Pits—I. Open Pits: Extraction, Transport, Cost—II. Underground Pits—Mining Laws. Chapter II., Preparation of the Clay: Weathering, Mixing Cleaning, Crushing and Pulverising—Crushing Cylinders and Mills, Pounding Machines—Damping: Damping Machines—Soaking, Shortening, Pugging: Horse and Steam Pug-Mills, Rolling Cylinders—Particulars of the Above Machines. Chapter III., Bricks: § 1, Manufacture—(1) Hand and Machine Moulding.—I. Machines Working by Compression; on Soft Clay, on Semi-Firm Clay, on Firm Clay, on Dry Clay.—II. Expression Machines: with Cylindrical Propellers, with Screw Propellers—Dies—Cutting-tables—Particulars of the Above Machines—General Remarks on the Choice of Machines—Types of Installations—Estimates—Plenishing, Hand and Steam Presses, Particulars—(2) Drying, by Exposure to Air, Without Shelter, and Under Sheds—Drying-rooms in Tiers, Closed Drying-rooms, in Tunnels, in Galleries—Detailed Estimates of the Various Drying-rooms, Comparison of Prices—Transport from the Machines to the Drying-rooms, Barrows, Trucks, Plain or with Shelves, Lifts—(3) Firing—I. In Clamps—II. In Intermittent Kilns. *A*, Open: *a*, using Wood; *b* Coal; *b'*, in Clamps; *b''*, Flame—*B*, Closed: *c*, Direct Flame; *c'*, Rectangular; *c''*, Round; *d*, Reverberatory—III. Continuous Kilns: *C*, with Solid Fuel: Round Kiln, Rectangular Kiln, Chimneys (Plans and Estimates)—*D*, With Gas Fuel, Fillard Kiln (Plans and Estimates), Schneider Kiln (Plans and Estimates), Water-gas Kiln—Heat Production of the Kilns; § 2, Dimensions, Shapes, Colours, Decoration, and Quality of Bricks—Hollow Bricks, Dimensions and Prices of Bricks, Various Shapes, Qualities—Various Hollow Bricks, Dimensions, Resistance, Qualities; § 3, Applications—History—Asia, Africa, America, Europe: Greek, Roman, Byzantine, Turkish, Romanesque, Gothic, Renaissance, Architecture—Architecture of the Nineteenth Century: in Germany, England, Belgium, Spain, Holland, France, America—Use of Bricks—Walls Arches Pavements

Flues, Cornices—Facing with Coloured Bricks—Balustrades. Chapter IV., Tiles: § 1, History; § 2, Manufacture—(1) Moulding, by Hand, by Machinery: Preparation of the Clay, Soft Paste, Firm Paste, Hard Paste—Preparation of the Slabs, Transformation into Flat Tiles, into Jointed Tiles—Screw, Cam and Revolver Presses—Particulars of Tile-presses—(2) Drying—Planchettes, Shelves, Drying-barrows and Trucks—(3) Firing—Divided Kilns—Installation of Mechanical Tileworks—Estimates; § 3, Shapes, Dimensions and Uses of the Principal Types of Tile—Ancient Tiles: Flat, Round, Roman, Flemish—Modern Tiles—With Vertical Interrupted Join: Gilardoni's, Martin's; Hooked, Boulet's Villa; with Vertical Continuous Join: Muller's, Alsace, Pantile—Foreign Tiles—Special Tiles—Ridge Tiles. Coping Tiles, Border Tiles, Frontons, Gutters, Antefixes, Membron, Angular—Roofing Accessories: Chimney-pots, Mitrons, Lanterns, Chimneys—Qualities of Tiles—Black Tiles—Stoneware Tiles—Particulars of Tiles. Chapter V., Pipes: I. Conduit Pipes—Manufacture—Moulding: Horizontal Machines, Vertical Machines, Worked by Hand and Steam—Particulars of these Machines—Drying—Firing—II. Chimney Flues—Ventiducts and "Boisseaux," "Waggons"—Particulars of these Products. Chapter VI., Quarries: 1, Plain Quarries of Ordinary Clay; 2, of Cleaned Clay—Machines, Cutting, Mixing, Polishing—Drying and Firing—Applications—Particulars of Quarries. Chapter VII., Terra-cotta: History—Manufacture—Application: Balustrades, Columns, Pilasters, Capitals, Friezes, Frontons, Medallions, Panels, Rose-windows, Ceilings—Appendix: Official Methods of Testing Terra-cottas.

Part II. **Made-up or Decorated Pottery.**—Chapter I., General Remarks on the Decoration of Pottery: Dips—Glazes: Composition, Colouring, Preparation, Harmony with Pastes—Special Processes of Decoration—Enamels, Opaque, Transparent, Colours, Underglaze, Over-glaze—Other Processes: Crackling, Mottled, Flashing, Metallic Iridescence, Lustres. Chapter II., Glazed and Enamelled Bricks—History: Glazing—Enamelling—Applications: Ordinary Enamelled Bricks, Glazed Stoneware, Enamelled Stoneware—Enamelled Tiles. Chapter III., Decorated Quarries: I. Paving Quarries—1, Decorated with Dips—2, Stoneware: *A*, Fired to Stoneware: *a*, of Slag Base—Applications; *b*, of Melting Clay—Applications—*B*, Plain or Incrusted Stoneware; *a*, of Special Clay (Stoke-on-Trent)—Manufacture—Application—*b*, of Felspar Base—Colouring, Manufacture, Moulding, Drying, Firing—Applications.—II. Facing Quarries—1, in Faïence—*A*, of Limestone Paste—*B*, of Silicious Paste—*C*, of Felspar Paste—Manufacture, Firing—2, of Glazed Stoneware—3, of Porcelain—Applications of Facing Quarries.—III. Stove Quarries—Preparation of the Pastes, Moulding, Firing, Enamelling, Decoration—Applications—Faïences for Fireplaces. Chapter IV., Architectural Decorated Pottery: § 1, Faïences; § 2, Stoneware; § 3, Porcelain. Chapter V., Sanitary Pottery: Stoneware Pipes: Manufacture, Firing—Applications—Sinks—Applications—Urinals, Seats and Pans—Applications—Drinking-fountains, Washstands.—Index.

A TREATISE ON THE CERAMIC INDUSTRIES. A

Complete Manual for Pottery, Tile and Brick Works. By EMILE BOURRY, Ingénieur des Arts et Manufactures. Translated from the French by WILTON P. RIX, Examiner in Pottery and Porcelain to the City and Guilds of London Technical Institute, Pottery Instructor to the Hanley School Board. Royal 8vo. 1901. Over 700 pp. Price 21s.; India and Colonies, 22s.; Other Countries, 23s. 6d.; strictly net.

Contents.

Part I., **General Pottery Methods.** Chapters I., Definition and History. Definitions and Classification of Ceramic Products—Historic Summary of the Ceramic Art.—II., Raw Materials of Bodies. Clays: Pure Clay and Natural Clays—Various Raw Materials: Analogous to Clay—Agglomerative and Agglutinative—Opening—Fusible—Refractory—Trials of Raw Materials.—III., Plastic Bodies. Properties and Composition—Preparation of Raw Materials: Disaggregation—Purification—Preparation of Bodies: By Plastic Method—By Dry Method—By Liquid Method.—IV., Formation. Processes of Formation: Throwing—Expression—Moulding by Hand, on the Jolley, by Compression, by Slip Casting—Slapping—Slipping.—V., Drying. Drying of Bodies—Processes of Drying: By Evaporation—By Aeration—By Heating—By Ventilation—By Absorption.—VI., Glazes. Composition and Properties—Raw Materials—Manufacture and Application.—VII., Firing. Properties of the Bodies and Glazes during Firing—Description of the Kilns—Working of the Kilns.—VIII., Decoration. Colouring Materials—Processes of Decoration.

Part II., **Special Pottery Methods.** Chapters IX., Terra Cottas. Classification: Plain Ordinary, Hollow, Ornamental, Vitrified, and Light Bricks—Ordinary and Black Tiles—Paving Tiles—Pipes—Architectural Terra Cottas—Vases, Statues and Decorative Objects—Common Pottery—Pottery for Water and Filters—Tobacco Pipes—Lustre Ware—Properties and Tests for Terra Cottas.—X., Fireclay Goods. Classification: Argillaceous, Aluminous, Carboniferous, Silicious and Basic Fireclay Goods—Fireclay Mortar (Pug)—Tests for Fireclay Goods.—XI., Faïences. Varnished Faïences—Enamelled Faïences—Silicious Faïences—Pipeclay Faïences—Pebble Work—Feldspathic Faïences—Composition, Processes of Manufacture and General Arrangements of Faïence Potteries.—XII., Stoneware. Stoneware Properly So-called: Paving Tiles—Pipes—Sanitary Ware—Stoneware for Food Purposes and Chemical Productions—Architectural Stoneware—Vases, Statues and other Decorative Objects—Fine Stoneware.—XIII., Porcelain. Hard Porcelain for Table Ware and Decoration, for the Fire, for Electrical Conduits, for Mechanical Purposes; Architectural Porcelain, and Dull or Biscuit Porcelain—Soft Phosphated or English Porcelain—Soft Vitreous Porcelain, French and New Sèvres—Argillaceous Soft or Seger's Porcelain—Dull Soft or Parian Porcelain—Dull Feldspathic Soft Porcelain.—**Index.**

THE ART OF RIVETING GLASS, CHINA AND EARTHENWARE.

By J. HOWARTH. Second Edition. 1900. Price 1s. net; by post, home or abroad, 1s. 1d.

Contents.

Tools and Materials Required—Wire Used for Rivets—Soldering Solution—Preparation for Drilling—Commencement of Drilling—Cementing—Preliminaries to Riveting—Rivets to Make—To Fix the Rivets—Through-and-through Rivets—Soldering—Tinning a Soldering-Iron—Perforated Plates, Handles, etc.—Handles of Ewers, etc.—Vases and Comports—Marble and Alabaster Ware—Decorating—How to Loosen Fast Decanter Stoppers—China Cements.

NOTES ON POTTERY CLAYS.

Their Distribution, Properties, Uses and Analyses of Ball Clays, China Clays and China Stone. By JAS. FAIRIE, F.G.S. 1901. 132 pp. Crown 8vo. Price 3s. 6d.; India and Colonies, 4s.; Other Countries, 4s. 6d.; strictly net.

Contents.

Definitions—Occurrence—Brick Clays—Fire Clays—Analyses of Fire Clays.—**Ball Clays**—Properties—Analyses—Occurrence—Pipe Clay—Black Clay—Brown Clay—Blue Clay—Dorsetshire and Devonshire Clays.—**China Clay** or Kaolin—Occurrence—Chinese Kaolin—Cornish Clays—Hensbarrow Granite—Properties, Analyses and Composition of China Clays—Method of Obtaining China Clay—Experiments with Chinese Kaolin—Analyses of Chinese and Japanese Clays and Bodies—Irish Clays.—**Chinese Stone**—Composition—Occurrence—Analyses.—Index.

PAINTING ON GLASS AND PORCELAIN AND ENAMEL PAINTING.

A Complete Introduction to the Preparation of all the Colours and Fluxes used for Painting on Porcelain, Enamel, Faience and Stoneware, the Coloured Pastes and Coloured Glasses, together with a Minute Description of the Firing of Colours and Enamels. On the Basis of Personal Practical Experience of the Condition of the Art up to Date. By FELIX HERMANN, Technical Chemist. With Eighteen Illustrations. 300 pp. Translated from the German second and enlarged Edition. 1897. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net.

Contents.

History of Glass Painting.—Chapters I., The Articles to be Painted: Glass, Porcelain, Enamel, Stoneware, Faience.—II., Pigments: 1, Metallic Pigments: Antimony Oxide, Naples Yellow, Barium Chromate, Lead Chromate, Silver Chloride, Chromic Oxide.—III., Fluxes: Fluxes, Felspar, Quartz, Purifying Quartz, Sedimentation, Quenching, Borax, Boracic Acid, Potassium and Sodium Carbonates, Rocaille Flux.—IV., Preparation of the Colours for Glass Painting.—V., The Colour Pastes.—VI., The Coloured Glasses.—VII., Composition of the Porcelain Colours.—VIII., The Enamel Colours: Enamels for Artistic Work.—IX., Metallic Ornamentation: Porcelain Gilding, Glass Gilding.—X., Firing the Colours: 1, Remarks on Firing: Firing Colours on Glass, Firing Colours on Porcelain: 2, The Muffle.—XI., Accidents occasionally Supervening during the Process of Firing.—XII., Remarks on the Different Methods of Painting on Glass, Porcelain, etc.—Appendix: Cleaning Old Glass Paintings.

Press Opinions.

"Will be found of much interest to the amateur."—*Art Amateur*, New York.

". . . The whole cannot fail to be both of service and interest to glass workers and to potters generally, especially those employed upon high-class work."—*Staffordshire Sentinel.*

"For manufacturers and students it will be a valuable work, and the recipes which appear on almost every page form a very valuable feature."—*Builders Journal.*

". . . Very careful instructions are given for the chemical and mechanical preparation of the colours used in glass-staining and porcelain-painting; indeed, to the china painter such a book as this should be of permanent value."—*Daily Chronicle.*

A TREATISE ON THE ART OF GLASS PAINTING.

Prefaced with a Review of Ancient Glass. By ERNEST R. SUFFLING. With One Coloured Plate and Thirty-seven Illustrations. Demy 8vo. 140 pp. 1902. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d. net.

Contents.

Chapters I., A Short History of Stained Glass.—II., Designing Scale Drawings.—III., Cartoons and the Cut Line.—IV., Various Kinds of Glass Cutting for Windows.—V., The Colours and Brushes used in Glass Painting.—VI., Painting on Glass, Dispersed Patterns.—VII., Diapered Patterns—Aciding—Firing.—VIII., Fret Lead Glazing.—Index.

A Reissue of

THE HISTORY OF THE STAFFORDSHIRE POTTERIES; AND THE RISE AND PROGRESS OF THE MANUFACTURE OF POTTERY AND PORCELAIN.

With References to Genuine Specimens, and Notices of Eminent Potters. By SIMEON SHAW. (Originally Published in 1829.) 265 pp. 1900. Demy 8vo. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Introductory Chapter showing the position of the Pottery Trade at the present time 1899).—Chapters I., **Preliminary Remarks.**—II., **The Potteries**, comprising Tunstall, Brownhills, Greenfield and New Field, Golden Hill, Latebrook, Green Lane, Burslem, Longport and Dale Hall, Hot Lane and Cobridge, Hanley and Shelton, Etruria, Stoke, Penkhull, Fenton, Lane Delph, Foley, Lane End.—III., **On the Origin of the Art**, and its Practice among the early Nations.—IV., **Manufacture of Pottery**, prior to 1700.—V., **The Introduction of Red Porcelain** by Messrs. Elers, of Bradwell, 1690.—VI., **Progress of the Manufacture** from 1700 to Mr. Wedgwood's commencement in 1760.—VII. **Introduction of Fluid Glaze.**—Extension of the Manufacture of Cream Colour.—Mr. Wedgwood's Queen's Ware.—Jasper, and Appointment of Potter to Her Majesty.—Black Printing.—VIII., **Introduction of Porcelain.** Mr. W. Littler's Porcelain.—Mr. Cookworthy's Discovery of Kaolin and Petuntse, and Patent.—Sold to Mr. Champion—resold to the New Hall Com.—Extension of Term.—IX., **Blue Printed Pottery.** Mr. Turner, Mr. Spode (1), Mr. Baddeley, Mr. Spode (2), Messrs. Turner, Mr. Wood, Mr. Wilson, Mr. Minton.—Great Change in Patterns of Blue Printed.—X., **Introduction of Lustre Pottery.** Improvements in Pottery and Porcelain subsequent to 1800.

Press Opinions.

"There is much curious and useful information in the work, and the publishers have rendered the public a service in reissuing it."—*Burton Mail.*

"Copies of the original work are now of considerable value, and the facsimile reprint now issued cannot but prove of considerable interest to all interested in the great industry."—*Derby Mercury.*

A Reissue of

THE CHEMISTRY OF THE SEVERAL NATURAL AND ARTIFICIAL HETEROGENEOUS COMPOUNDS USED IN MANUFACTURING PORCELAIN, GLASS AND POTTERY. By SIMEON SHAW.

(Originally published in 1837.) 750 pp. 1900. Royal 8vo. Price 14s.; India and Colonies, 15s.; Other Countries, 16s. 6d.; strictly net.

Contents.

PART I., ANALYSIS AND MATERIALS.—Chapters I., **Introduction:** Laboratory and Apparatus; **Elements:** Combinative Potencies, Manipulative Processes for Analysis and Reagents, Pulverisation, Blow-pipe Analysis, Humid Analysis, Preparatory Manipulations, General Analytic Processes, Compounds Soluble in Water, Compounds Soluble only in Acids, Compounds (Mixed) Soluble in Water, Compounds (Mixed) Soluble in Acids, Compounds (Mixed) Insoluble, Particular Analytic Processes.—II., **Temperature:** Coal, Steam Heat for Printers' Stoves.—III., **Acids and Alkalies:** Boracic Acid, Muriatic Acid, Nitric Acid, Sulphuric Acid, Potash, Soda, Lithia, Calculation of Chemical Separations.—IV., **The Earths:** Alumine, Clays, Silica, Flint, Lime, Plaster of Paris, Magnesia, Barytes, Felspar, Grauen (or China Stone), China Clay, Chert.—V., **Metals:** Reciprocal Combinative Potencies of the Metals, Antimony, Arsenic, Chromium, Green Oxide, Cobalt, Chromic Acid, Humid Separation of Nickel from Cobalt, Arsenite of Cobalt, Copper, Gold, Iron, Lead, Manganese, Platinum, Silver, Tin, Zinc.

PART II., SYNTHESIS AND COMPOUNDS.—Chapters I., Sketch of the Origin and Progress of the Art.—II., **Science of Mixing:** Scientific Principles of the Manufacture, Combinative Potencies of the Earths.—III., **Bodies:** Porcelain—Hard, Porcelain—Fritted Bodies, Porcelain—Raw Bodies, Porcelain—Soft, Fritted Bodies, Raw Bodies, Stone Bodies, Ironstone, Dry Bodies, Chemical Utensils, Fritted Jasper, Fritted Pearl, Fritted Drab, Raw Chemical Utensils, Raw Stone, Raw Jasper, Raw Pearl, Raw Mortar, Raw Drab, Raw Brown, Raw Fawn, Raw Cane, Raw Red Porous, Raw Egyptian, Earthenware, Queen's Ware, Cream Colour, Blue and Fancy Printed, Dipped and Mocha, Chalky, Rings, Stilts, etc.—IV., **Glazes:** Porcelain—Hard Fritted, Porcelain—Soft Fritted, Porcelain—Soft Raw, Cream Colour Porcelain, Blue Printed Porcelain, Fritted Glazes, Analysis of Fritt, Analysis of Glaze, Coloured Glazes, Dips, Smears and Washes; **Glasses:** Flint Glass, Coloured Glasses, Artificial Garnet, Artificial Emerald, Artificial Amethyst, Artificial Sapphire, Artificial Opal, Plate Glass, Crown Glass, Broad Glass, Bottle Glass, Phosphoric Glass, British Steel Glass, Glass-Staining and Painting, Engraving on Glass, Dr. Faraday's Experiments.—V., **Colours:** Colour Making, Fluxes or Solvents, Components of the Colours; **Reds, etc., from Gold**, Carmine or Rose Colour, Purple, Reds, etc., from Iron, Blues, Yellows, Greens, Blacks, White, Silver for Burnishing, Gold for Burnishing, Printer's Oil, Lustres.

PART III., TABLES OF THE CHARACTERISTICS OF CHEMICAL SUBSTANCES.

Press Opinions.

". . . There is an excellent historical sketch of the origin and progress of the art of pottery which shows the intimate knowledge of classical as well as (the then) modern scientific literature possessed by the late Dr. Shaw."—*Glasgow Herald.*

"The historical sketch of the origin and progress of pottery is very interesting and instructive. The science of mixing is a problem of great importance, and the query how the natural products, alumina and silica can be compounded to form the best wares may be solved by the aid of chemistry instead of by guesses, as was formerly the case. This portion of the book may be most suggestive to the manufacturer, as also the chapters devoted to the subject of glazes, glasses and colours."—*Birmingham Post.*

"Messrs. Scott, Greenwood & Co. are doing their best to place before the pottery trades some really good books, and their spirited enterprise is worthy of encouragement, for the utility of technical literature bearing upon the practical side of potting goes without saying. . . . They are to be congratulated on their enterprise in republishing it."—*Staffordshire Sentinel.*

Paper Making.

THE DYEING OF PAPER PULP. A Practical Treatise for the use of Papermakers, Paperstainers, Students and others. By JULIUS ERFURT, Manager of a Paper Mill. Translated into English and Edited with Additions by JULIUS HÜBNER, F.C.S., Lecturer on Papermaking at the Manchester Municipal Technical School. With Illustrations and **157 patterns of paper dyed in the pulp.** Royal 8vo, 180 pp. 1901. Price 15s.; India and Colonies, 16s.; Other Countries, 20s.; strictly net. Limited edition.

Contents.

I., **Behaviour of the Paper Fibres during the Process of Dyeing, Theory of the Mordant.**—II., **Colour Fixing Mediums (Mordants).**—III., **Influence of the Quality of the Water Used.**—IV., **Inorganic Colours.**—V., **Organic Colours.**—VI., **Practical Application of the Coal Tar Colours according to their Properties and their Behaviour towards the Different Paper Fibres.**—VII., **Dyed Patterns on Various Pulp Mixtures.**—**Dyeing to Shade.**—Index.

Press Opinions.

"The book is one that is of value to every one connected with the colouring of paper."—*Paper Trade Journal.*

"The great feature of the volume is undoubtedly the series of actual patterns of dyed papers, 157 in all—twelve of which, made in England, have been added to the original German series. Detailed formulæ are given for the preparation of the pulp for each, and the tints of the samples practically form a key, by means of which the accuracy of the student's or practitioner's experiments can be tested. . . ."—*World's Paper Trade Review.*

Enamelling on Metal.

ENAMELS AND ENAMELLING. An Introduction to the Preparation and Application of all Kinds of Enamels for Technical and Artistic Purposes. For Enamel Makers, Workers in Gold and Silver, and Manufacturers of Objects of Art. By PAUL RANDAU. Translated from the German. With Sixteen Illustrations. 180 pp. 1900. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net.

Contents.

I., Introduction.—II., Composition and Properties of Glass.—III., Raw Materials for the Manufacture of Enamels.—IV., Substances Added to Produce Opacity.—V., Fluxes.—VI., Pigments.—VII., Decolorising Agents.—VIII., Testing the Raw Materials with the Blow-pipe Flame.—IX., Subsidiary Materials.—X., Preparing the Materials for Enamel Making.—XI., Mixing the Materials.—XII., The Preparation of Technical Enamels, The Enamel Mass.—XIII., Appliances for Smelting the Enamel Mass.—XIV., Smelting the Charge.—XV., Composition of Enamel Masses.—XVI., Composition of Masses for Ground Enamels.—XVII., Composition of Cover Enamels.—XVIII., Preparing the Articles for Enamelling.—XIX., Applying the Enamel.—XX., Firing the Ground Enamel.—XXI., Applying and Firing the Cover Enamel or Glaze.—XXII., Repairing Defects in Enamelled Ware.—XXIII., Enamelling Articles of Sheet Metal.—XXIV., Decorating Enamelled Ware.—XXV., Specialities in Enamelling.—XXVI., Dial-plate Enamelling.—XXVII., Enamels for Artistic Purposes, Recipes for Enamels of Various Colours.—Index.

Press Opinions.

"Should prove of great service to all who are either engaged in or interested in the art of enamelling."—*Jewellers and Watchmakers' Trade Advertiser.*

"I must inform you that this is the best book ever I have come across on enamels, and it is worth double its cost."—J. MINCHIN, Jr., Porto, Portugal, *22nd July*, 1900.

"This is a very useful and thoroughly practical treatise, and deals with every branch of the enameller's art."—*Invention.*

THE ART OF ENAMELLING ON METAL. By W. NORMAN BROWN. Twenty-eight Illustrations. Crown 8vo. 60 pp. 1900. Price 2s. 6d.; Abroad, 3s.; strictly net.

Contents.

Chapters I., History—Cloisonné—Champs Levé—Translucent Enamel—Surface Painted Enamels.—II., Cloisonné—Champs Levés—Translucent—Painted.—III., Painted Enamel—Apparatus—Furnaces and Muffles for Firing.—IV., The Copper Base or Plate—Planishing—Cloisons—Champ Levé Plates.—V., Enamels—Trituration—Washing—Coating a Plate with Enamel—Firing Ordinary Plaques for Painting—Designing—Squaring off.—VI., Designs for Cloisonné—Designs for Painted Enamels—Technical Processes—Brushes, etc.,—Colours—Grisaille—Full-coloured Designs.

Press Opinion.

"The information conveyed in *The Art of Enamelling on Metal* is as complete as can be expected in a manual of ordinary length, and is quite ample in all respects to start students in a most interesting branch of decorative art."—*Hardware Metals and Machinery.*

Books on Textile and Dyeing Subjects.

THE TECHNICAL TESTING OF YARNS AND TEXTILE FABRICS. With Reference to Official Specifications. Translated from the German of Dr. J. HERZFELD. Second Edition. Sixty-nine Illustrations. 200 pp. Demy 8vo. 1902. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net.

Contents.

Yarn Testing. III., **Determining the Yarn Number.**—IV., **Testing the Length of Yarns.**—V., **Examination of the External Appearance of Yarn.**—VI., **Determining the Twist of Yarn and Twist.**—VII., **Determination of Tensile Strength and Elasticity.**—VIII., **Estimating the Percentage of Fat in Yarn.**—IX., **Determination of Moisture** (Conditioning).—**Appendix**

Press Opinions.

"It would be well if our English manufacturers would avail themselves of this important addition to the extensive list of German publications which, by the spread of technical information, contribute in no small degree to the success, and sometimes to the supremacy, of Germany in almost every branch of textile manufacture."—*Manchester Courier.*

"This is probably the most exhaustive book published in English on the subject."—*Textile Recorder.*

"A careful study of this book enables one to say with certainty that it is a standard work on the subject."—*Glasgow Herald.*

". . . For the first time all the data relating to both physical and chemical tests as used throughout the whole of the textile industry, so that not only the commercial and textile chemist, who has frequently to reply to questions on these matters, but also the practical manufacturer of textiles and his subordinates, whether in spinning, weaving, dyeing, and finishing, are catered for. . . . The book is profusely illustrated, and the subjects of these illustrations are clearly described."—*Textile Manufacturer.*

DECORATIVE AND FANCY TEXTILE FABRICS. With Designs and Illustrations. By R. T. LORD. A Valuable Book for Manufacturers and Designers of Carpets, Damask, Dress and all Textile Fabrics. 200 pp. 1898. Demy 8vo. 132 Designs and Illustrations. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., A Few Hints on Designing Ornamental Textile Fabrics.—II., A Few Hints on Designing Ornamental Textile Fabrics (continued).—III., A Few Hints on Designing Ornamental Textile Fabrics (continued).—IV., A Few Hints on Designing Ornamental Textile Fabrics (continued).—V., Hints for Ruled-paper Draughtsmen.—VI., The Jacquard Machine.—VII., Brussels and Wilton Carpets.—VIII., Tapestry Carpets.—IX., Ingrain Carpets.—X., Axminster Carpets.—XI., Damask and Tapestry Fabrics.—XII., Scarf Silks and Ribbons.—XIII., Silk Handkerchiefs.—XIV., Dress Fabrics.—XV., Mantle Cloths.—XVI., Figured Plush.—XVII., Bed Quilts.—XVIII., Calico Printing.

Press Opinions.

"The book can be strongly recommended to students and practical men."—*Textile Colourist.*

"Those engaged in the designing of dress, mantle tapestry, carpet and other ornamental textiles will find this volume a useful work of reference."—*Leeds Mercury.*

"To be commended as a model manual."—*Dundee Advertiser.*

"Designers especially, who desire to make progress in their calling, will do well to take the hints thrown out in the first four chapters on 'Designing Ornamental Textile Fabrics'."—*Nottingham Daily Guardian.*

POWER-LOOM WEAVING AND YARN NUMBERING,

According to Various Systems, with Conversion Tables. An Auxiliary and Text-book for Pupils of Weaving Schools, as well as for Self-Instruction and for General Use by those engaged in the Weaving Industry. Translated from the German of ANTHON GRUNER. **With Twenty-six Diagrams in Colours.** 150 pp. 1900. Crown 8vo. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

I., **Power-Loom Weaving in General.** Various Systems of Looms.—II., **Mounting and Starting the Power-Loom.** English Looms.—Tappet or Treadle Looms.—Dobbies.—III., **General Remarks on the Numbering, Reeling and Packing of Yarn.—Appendix.—Useful Hints.** Calculating Warps.—Weft Calculations.—Calculations of Cost Price in Hanks.

Press Opinions.

"A long-felt want in the weaving industry."—*Belfast Evening Telegraph.*

"The author has dealt very practically with the subject."—*Bradford Daily Telegraph.*

"The book . . . should prove invaluable to the student."—*Cotton Factory Times.*

"It is a capital text-book for use in the weaving schools or for self-instruction, while all engaged in the weaving industry will find its suggestions helpful."—*Northern Daily Telegraph.*

"Yarn numbering according to various systems, with conversion tables and numerous coloured diagrams, materially assist to a clear comprehension of the subject."—*Northern Whig.*

"The 'inside' managers of our textile mills in which the work is complex or greatly varied, and where yarns of different materials are in use, will find this work convenient for reference."—*Textile Mercury.*

"The author attempts to fill a gap in weaving literature caused by the neglect of many obscure points connected with the industry."—*Cheshire County News.*

"It is clear and concise, and gives just that knowledge in quality and amount which any student of the weaving industry ought to consider as a minimum necessary for his thorough comprehension of his future profession."—*North British Daily Mail.*

". . . The work should prove of much value, as it is in every sense practical, and is put before the reader in such a clear manner that it can be easily understood."—*Textile Industries.*

"The smallest details of loom-setting are entered into, and a full explanation of problems, which are a source of anxiety to many engaged in overlooking, is given. Students will find the work an admirable text-book, and all who are interested in weaving will see in it a valuable addition to the literature on this subject."—*Bradford Observer.*

THE CHEMICAL TECHNOLOGY OF TEXTILE FIBRES: Their Origin, Structure, Preparation, Washing, Bleaching, Dyeing, Printing and Dressing.

By Dr. GEORG VON GEORGIEVICS. Translated from the German by CHARLES SALTER. 320 pp. Forty-seven Illustrations. Royal 8vo. 1902. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s. net.

Contents.

Chapters I., **The Textile Fibres.**—Artificial Fibres—Mineral Fibres—Vegetable Fibres—Cellulose—Cotton—Bombax Cotton—Vegetable Silk—Flax—Hemp—Jute—Ramie, Rhea, China Grass, Nettle Fibre—Distinguishing Tests for the Various Fibres—Animal Fibres: Silk—Animal Hairs—Sheep's Wool—Goat Wool and Camel Wool—Artificial Wool (Wool Substitutes)—Conditioning.—II., **Washing, Bleaching, Carbonising.**—Washing and Bleaching (Definition)—Bleaching Agents—Cotton Bleaching—Linen Bleaching—Jute Bleaching—Hemp Bleaching—Ramie Bleaching—Scouring and Bleaching Silk—Washing and Bleaching Wool—Blueing or White Dyeing—Carbonising.—III., **Mordants and Mordanting.**—Mordants: Mordanting Wool—Mordanting Silk—Mordanting Cotton—Alumina Mordants—Iron Mordants—Chrome Mordants—Tin Mordants—Copper and other Mordants—The Fixing Agents (Acid Mordants): Tannic Acids—Oleic Acids.—IV., **Dyeing.**—(1) Theory of Colour: Combination of Colours: Dyeing to Pattern—(2) Theory of Dyeing—(3) Classification of Dye Stuffs: Methods of Dyeing—Application of Acid Dye Stuffs—Application of Basic Dye Stuffs—Application of Direct or Substantive Cotton Dyes—Application of the Mordant Dyes: Dyeing with Cochineal—Black and Blue Dyeings with Logwood on Wool—Turkey-Red Dyeing—Dyeing with Catechu—Black-Dyeing Cotton with Logwood—Application of the Vat Dyes—Application of the Developing Dyes—(4) Dyeing on a Manufacturing Scale: Selection of Dye Stuffs for Dyeing—Silk Dyeing—Wool Dyeing—Cotton Dyeing—Dyeing Mixed Fabrics—(5) Sample Dyeings, Colorimetric Determinations, Reactions of Dye Stuffs on the Fibre, Tests for Fastness—V., **Printing.**—Hand Printing—The Perrotine Press—The Cylinder Press—Calico Printing: (1) Reproduction of Pattern by Direct Printing: Thickening Agents—Employment of Mordant Dye Stuffs, Basic, Albumin, Direct, Developing, Vat, Acid—Treatment of the Goods when Printed—(2) Combined Printing and Dyeing—(3) Discharge Style Printing: Discharging the Mordant—Discharging Antimony Tannate—Discharging the Finished Dye—Turkey-Red Discharge Style—(4) Reserve Style Printing—(5) Topping Printing—Wool Printing—Silk Printing—Printing Yarns, Warps, and Combed Sliver.—VI., **Dressing and Finishing.**—Dressing and Finishing—Substances used in Finishing: (1) Starch, Gum, etc.—(2) Fatty Substances—(3) Hygroscopic Materials—(4) Loading Ingredients—(5) Colouring for the Dressing Preparations—(6) Metals or their Sulphites—(7) Waterproofing—(8) Fireproofing—(9) Antiseptics for Prevention of Mould—Application of Dressings—Drying—Stretching—Finishing: Shearing, Damping, Calendering, Beetling, Moiré or Watered Effects, Stamping—Finishing Woollens.—Index.

COLOUR: A HANDBOOK OF THE THEORY OF COLOUR.

By GEORGE H. HURST, F.C.S. **With Ten Coloured Plates** and Seventy-two Illustrations. 160 pp. Demy 8vo. 1900. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., **Colour and its Production.** Light, Colour, Dispersion of White Light, Methods of Producing the Spectrum, Glass Prism and Diffraction Grating Spectroscopes, The Spectrum, Wave Motion of Light, Recomposition of White Light, Hue, Luminosity, Purity of Colours, The Polariscope, Phosphorescence, Fluorescence, Interference.—II., **Cause of Colour in Coloured Bodies.** Transmitted Colours, Absorption Spectra of Colouring Matters.—III., **Colour Phenomena and Theories.** Mixing Colours, White Light from Coloured Lights, Effect of Coloured Light on Colours, Complementary Colours, Young-Helmholtz Theory, Brewster Theory, Supplementary Colours, Maxwell's Theory, Colour Photography.—IV., **The Physiology of Light.** Structure of the Eye, Persistence of Vision, Subjective Colour Phenomena, Colour Blindness.—V., **Contrast.** Contrast, Simultaneous Contrast, Successive Contrast, Contrast of Tone, Contrast of Colours, Modification of Colours by Contrast, Colour Contrast in Decorative Design.—VI., **Colour in Decoration and Design.** Colour Harmonies, Colour Equivalents, Illumination and Colour, Colour and Textile Fabrics, Surface Structure and Colour.—VII., **Measurement of Colour.** Colour Patch Method, The Tintometer, Chromometer.

Press Opinions.

"This useful little book possesses considerable merit."—*Birmingham Post.*

"It will be found to be of direct service to the majority of dyers, calico printers and colour mixers, to whom we confidently recommend it."—*Chemical Trade Journal.*

"It is thoroughly practical, and gives in simple language the why and wherefore of the many colour phenomena which perplex the dyer and the colourist."—*Dyer and Calico Printer.*

TEXTILE RAW MATERIALS AND THEIR CONVERSION INTO YARNS.

(The Study of the Raw Materials and the Technology of the Spinning Process.) Text-book for Textile, Trade and Higher Technical Schools. By JULIUS ZIPSER. Translated from German by CHARLES SALTER. 302 Illustrations. 480 pp. Demy 8vo. 1901. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net.

Contents.

Introduction.

PART I.—The Raw Materials Used in the Textile Industry.

GROUP I. MINERAL RAW MATERIALS. Asbestos—Glass—Metals.

GROUP II. VEGETABLE RAW MATERIALS. Seed Fibres—Cotton—Bombax Wool—Asclepias Wool—Poplar, Cotton Grass and Bulrush Wool—Stem Fibres—Flax—Hemp—Jute—Nettle Fibres—Sunn Hemp—Leaf Fibres—New Zealand Hemp—Manila Hemp—Sisal and Domingo Hemp—Aloe Fibre—Pineapple Fibre—Vegetable Wool—Fruit Fibres—Cocoanut Fibre—Other Vegetable Raw Materials employed in Weaving—Straw—Wood—Cane—Caoutchouc.

GROUP III. ANIMAL RAW MATERIALS. Animal Wool and Hair—Sheep's Wool—Goat Wool—Camel Wool—Llama and similar Wools—Cow Hair—Poodle Hair—Hare, Rabbit, Cat and Beaver Fur—Horse Hair—Bristles—Silk—Natural Silk—Artificial Silk—Byssus Silk—Detection and Estimation of Textile Raw Materials in Yarns and Fabrics—Characteristics of Mineral Raw Materials—Detecting and Methods of separating Vegetable and Animal Raw Materials in general—The Combustion Test—The Mandarin Test—The Picric Acid Test—The Sulphuric Acid Test—The Alkali Test—Differentiation of Animal and Vegetable Fibres in detail—Characteristics of Cotton—Characteristics of Flax—Characteristics of Sheep's Wool—Characteristics of True Silk—Characteristics of Artificial Silk—Determining the Constituents of Textile Fabrics—The Detection of Cotton in Linen Fabrics—The Detection of Cotton in Woollen Fabrics—The Detection of Cotton in Silk Fabrics—The Detection of Wool in Silk Fabrics—The Detection of Wild Silk in True Silk Fabrics—The Detection of Artificial Silk in Silk Fabrics—The Detection of Byssus Silk in Silk Fabrics.

PART II.—The Technology of Spinning or the Conversion of Textile Raw Materials into Yarn.

Spinning—Sequence of Operations in Spinning—General Observations on the Machinery and Process of Spinning—Fine Spinning Machines—Requisite Properties for a Well-spun Thread.

GENERAL REVIEW OF THE VARIOUS BRANCHES OF THE SPINNING PROCESS.

GROUP I. SPINNING VEGETABLE RAW MATERIALS. Cotton Spinning—Preparatory Processes—Mixing—Opening and Cleaning—Carding—Combing—Drawing and Doubling—Roving—Roving Frames producing a Permanent Twist—Machines producing Temporary Twist—Fine Spinning—The Throstle or Water Frame—The Mule Frame—Supplementary Treatment: Finishing—Finishing Processes producing no change in the Character of the Yarn—Converting Yarns into New Forms—Additional Finishing Processes—Packing—Installation of a Cotton Mill—Humidifiers—Spinning Waste Cotton and Waste Cotton Yarns—Preliminary Operations

—Carding—Slubbing—Fine Spinning—Supplementary and Finishing Operations—Flax Spinning—Preparatory Treatment—Gilling—Doubling and Drawing—Roving—The Roving Frame—Fine Spinning—Supplementary Treatment—Operations leaving the Yarn unchanged—Operations for producing New Combinations of Threads—Packing—Tow Spinning—Preparatory Treatment—Roving—Fine Spinning—Hemp Spinning—Spinning Hackled or Line Hemp—Spinning Hemp Tow String—Jute Spinning—Spinning Jute Line Yarn—Spinning Jute Tow Yarns—Supplementary Treatment—The Production of Mixed Yarns—Utilising Jute Waste.

PART III.—Spinning Animal Raw Materials.

Spinning Carded Woollen Yarn—Preparatory Treatment—Scouring, Washing and Rinsing—Draining and Drying the Wool—Burr Extraction—Opening and Willowing—Oiling the Wool—Carding—Condensing—Belt Condensers—Steel Band Condenser—Fine Spinning—The Mule—The Throstle Frame—Supplementary Treatment—Supplementary Treatment leaving the Yarn unaltered—Treatment with a view to producing Novel Effects—Finishing Yarn—Packing Yarn—Worsted Spinning—Manufacture of True Worsted Yarn—Preliminary Treatment—Sorting—Steeping, Washing and Rinsing—Drying—Oiling—Carding—Gilling—Combing—Drawing—Smoothing—Drawing and Slubbing—Roving—Fine Spinning—The Worsted Mule Frame—Worsted Throstle Frames—Supplementary Treatment—Processes leaving the Yarn unchanged—Producing New Types of Yarn—Finishing Worsted Yarn—Packing—Semi-Worsted Yarns—Artificial Wool or Shoddy Spinning—Shoddy and Mungo Manufacture—Cleaning the Rags—Sorting the Rags—Trimming the Rags—Scouring—Disintegration—Extract Wool—Shaking—Scouring—Carbonising—Disintegration—Spinning Shoddy and other Wool Substitutes—Spinning Waste Silk—Chappe Silk—Preliminary Treatment—Sorting—Steeping—Maceration—Scouring and Beetling—Drying—Sprinkling—Beating—Opening—Dressing—Spreading—Doubling and Drawing—Slubbing and Roving—Fine Spinning—Supplementary Operations—Operations leaving the Yarn unaltered—Producing New Forms of Yarn—Finishing off Chappe Silk—Packing—Bourette Spinning.—Index.

DYERS' MATERIALS: An Introduction to the Examination, Evaluation and Application of the most important Substances used in Dyeing, Printing, Bleaching and Finishing. By PAUL HEERMAN, Ph.D. Translated from the German by ARTHUR C. WRIGHT, M.A. (Oxon.), B.Sc. (Lond.). With Two Plates, containing Twenty-four Illustrations. Crown 8vo. 150 pp. 1901. Price 5s.; India and Colonies, 5s. 6d.; Other Countries, 6s; strictly net.

Contents.

Chapter I., General: Table I., *Indicators—Standard Solutions.*—Table II., *Solutions and Reagents in General Use.*—Chapter II., Primary Materials: *Water—Textile Fibres.* Chapter III., Inorganic Materials: *Hydrochloric Acid—Chlorides* of Sodium, Magnesium, Ammonium, Barium, Zinc, Copper, Manganese and Aluminium, Stannous Chloride, Stannic Chloride, Tin Spirits, Chromium Chloride—*Fluorides and Bifluorides*, Alkaline Bifluorides, Chromium Fluoride, Chromium Oxyfluoride, Copper Fluoride, Antimony Fluoride, Aniline Hydrofluoride, Antimony Fluoride, Double Salts—*Sulphuric Acid*, Fuming or Nordhausen Sulphuric Acid—*Sulphates*, Sodium Sulphate, Sodium Bisulphate, Calcium Sulphate, Magnesium Sulphate, Lead Sulphate, Ferrous Sulphate, Aluminium Sulphate, Ferric Sulphate, Copper Sulphate, Alums—*Nitric Acid and Nitrates:* Nitric Acid, Sodium, Silver, Lead, Ferrous, Ferric and Rarer Nitrates—*Chlorine-Oxygen Compounds:* Bleaching Powder, Alkaline Hypochlorites, other Hypochlorites, Potassium, Sodium, Aluminium, Chromium and Aniline Chlorates—*Sulphite Compounds*: Sulphurous Acid, Sulphites, Sodium Bisulphite, Hydro- or Hyposulphurous Acid, Hydro- or Hyposulphites, Sodium Thiosulphate—*Miscellaneous Compounds*: Sodium Nitrite, Sodium Phosphate, Water-glass, Sodium Arsenate, Sodium Tungstate, Sodium Stannate, Sodium Aluminate, Borax, Potassium Permanganate, Potassium Bichromate, Sodium Bichromate, Vanadates—*Alkalies*: Ammonia, Ammonium Salts, Caustic Soda, Caustic Potash, Sodium Carbonate, Calcium Carbonate—*Peroxides*: Hydrogen Peroxide, Barium Peroxide, Sodium Peroxide—*Zinc Dust.*—Chapter IV., Organic Compounds: *Fatty Acids and Their Salts*—Acetic Acid, Acetates, Ferrous Acetate, Oxalic Acid and Oxalates, Tartaric Acid, Tartar, Tartar Emetic, Citric Acid, Lactic Acid—*Cyanogen Compounds*: Sulphocyanides, Potassium Ferrocyanide, Potassium Ferricyanide—*Derivatives of the Fats*: Soap, "Boiled-off Liquor," Turkey Red Oil—*Tannins—Aniline and Analine Salts—Thickening and Stiffening Materials*: Starch, Prepared and Soluble Starch, Dextrine, Gum Arabic, Gum Senegal, Gum Tragacanth, Glue, Size—*Dyes.*—Appendix: Atomic Weights of the Elements—Molecular Weights of Certain Compounds—Gravimetric Equivalents—Volumetric Equivalents.—Plate I., Microscopic Appearance of the Textile Fibres (11 Illustrations).—Plate II., Microscopic Appearance of the Different Varieties of Starch (13 Illustrations).—Index.

Press Opinions.

"To those engaged in any branches of dyeing, printing, bleaching and finishing it ought to prove a valuable addition to existing works."—*Textile Industries.*

"Cannot fail to be of the greatest value."—*Huddersfield Examiner.*

THE COLOUR PRINTING OF CARPET YARNS. A Useful Manual for Colour Chemists and Textile Printers. By DAVID PATERSON, F.C.S. Seventeen Illustrations. 132 pp. Demy 8vo. 1900. Price 7s. 6d.; India and Colonies, 8s. Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., Structure and Constitution of Wool Fibre.—II., Yarn Scouring.—III., Scouring Materials.—IV., Water for Scouring.—V., Bleaching Carpet Yarns.—VI., Colour Making for Yarn Printing.—VII., Colour Printing Pastes.—VIII., Colour Recipes for Yarn Printing.—IX., Science of Colour Mixing.—X., Matching of Colours.—XI., "Hank" Printing.—XII., Printing Tapestry Carpet Yarns.—XIII., Yarn Printing.—XIV., Steaming Printed Yarns.—XV., Washing of Steamed Yarns.—XVI., Aniline Colours Suitable for Yarn Printing.—XVII., Glossary of Dyes and Dye-wares used in Wood Yarn Printing.—Appendix.

Press Opinions.

"The book is worthy the attention of the trade."—*Worcester Herald.*

"The treatise is arranged with great care, and follows the processes described in a manner at once clear and convincing."—*Glasgow Record.*

"A most useful manual dealing in an intelligible and interesting manner with the colour printing of carpet yarns."—*Kidderminster Times.*

"The author has evidently strained every effort in order to make his work the standard guide of its class."—*Leicester Post.*

"The book, which is admirably printed and illustrated, should fulfil the need of a practical guide in the colour printing of carpet yarns.—*Nottingham Express.*

"The subject is very exhaustively treated in all its branches. . . ."—*Northern Whig.*

"It gives an account of its subject which is both valuable and instructive."—*Scotsman.*

"The work shows a thorough grasp of the leading characteristics as well as the minutæ of the industry, and gives a lucid description of its chief departments. . . . As a text-book in technical schools where this branch of industrial education is taught, the book is valuable."—*Dundee Courier.*

"The book bears every mark of an extensive practical knowledge of the subject in all its bearings, and supplies a real want in technical literature."—*Dyer and Calico Printer.*

"It is thoroughly practical, and contains much information which has not hitherto appeared in book form."—*Journal of the Society of Dyers and Colourists.*

A PRACTICAL TREATISE ON THE BLEACHING OF LINEN AND COTTON YARN AND FABRICS.

By L. TAILFER, Chemical and Mechanical Engineer. Translated from the French by JOHN GEDDES McINTOSH, Lecturer on Chemical Technology, London. Demy 8vo. 303 pp. Twenty Illusts. 1901. Price 12s. 6d.; India and Colonies, 13s. 6d.; Other Countries, 15s.; strictly net.

Contents.

Chapter I. General Considerations on Bleaching. Chapter II. Steeping. Chapter III. Washing: Its End and Importance—Roller Washing Machines—Wash Wheel (Dash Wheel)—Stocks or Wash Mill—Squeezing. Chapter IV. Lye Boiling—Lye Boiling with Milk of Lime—Lye Boiling with Soda Lyes—Description of Lye Boiling Keirs—Operations of Lye Boiling—Concentration of Lyes. Chapter V. Mather and Platt's Keir—Description of the Keir—Saturation of the Fabrics—Alkali used in Lye Boiling—Examples of Processes. Chapter VI. Soap—Action of Soap in Bleaching—Quality and Quantity of Soaps to use in the Lye—Soap Lyes or Scalds—Soap Scouring Stocks. Chapter VII. Bleaching on Grass or on the Bleaching Green or Lawn. Chapter VIII. Chemicking—Remarks on Chlorides and their Decolourising Action—Chemicking Cisterns—Chemicking—Strengths, etc. Chapter IX. Sours—Properties of the Acids—Effects Produced by Acids—Souring Cisterns. Chapter X. Drying—Drying by Steam—Drying by Hot Air—Drying by Air. Chapter XI. Damages to Fabrics in Bleaching—Yarn Mildew—Fermentation—Iron Rust Spots—Spots from Contact with Wood—Spots incurred on the Bleaching Green—Damages arising from the Machines. Chapter XII. Examples of Methods used in Bleaching—Linen—Cotton. Chapter XIII. The Valuation of Caustic and Carbonated Alkali (Soda) and General Information Regarding these Bodies—Object of Alkalimetry—Titration of Carbonate of Soda—Comparative Table of Different Degrees of Alkalimetrical Strength—Five Problems relative to Carbonate of Soda—Caustic Soda, its Properties and Uses—Mixtures of Carbonated and Caustic Alkali—Note on a Process of Manufacturing Caustic Soda and Mixtures of Caustic and Carbonated Alkali Soda). Chapter XIV. Chlorometry—Titration—Wagner's Chlorometric Method—Preparation of Standard Solutions—Apparatus for Chlorine Valuation—Alkali in Excess in Decolourising Chlorides. Chapter XV. Chlorine and Decolourising Chlorides—Synopsis—Chlorine—Chloride of Lime—Hypochlorite of Soda—Brochoki's Chlorozone—Various Decolourising Hypochlorites—Comparison of Chloride of Lime and Hypochlorite of Soda Chapter XVI. Water—Qualities of Water—Hardness—Dervaux's Purifier—Testing the Purified Water—Different Plant for Purification—Filters. Chapter XVII. Bleaching of Yarn—Weight of Yarn—Lye Boiling—Chemicking—Washing—Bleaching of Cotton Yarn. Chapter XVIII. The Installation of a Bleach Works—Water Supply—Steam Boilers—Steam Distribution Pipes—Engines—Keirs—Washing Machines—Stocks—Wash Wheels—Chemicking and Souring Cisterns—Various—Buildings. Chapter XIX. Addenda—Energy of Decolourising Chlorides and Bleaching by Electricity and Ozone—Energy of Decolourising Chlorides—Chlorides—Production of Chlorine and Hypochlorites by Electrolysis—Lunge's Process for increasing the intensity of the Bleaching Power of Chloride of Lime—Trilfer's Process for Removing the Excess of Lime or Soda from Decolourising Chlorides—Bleaching by Ozone.

THE SCIENCE OF COLOUR MIXING. A Manual intended for the use of Dyers, Calico Printers and Colour Chemists. By DAVID PATERSON, F.C.S. Forty-one Illustrations, **Five Coloured Plates, and Four Plates showing Eleven Dyed Specimens of Fabrics.** 132 pp. Demy 8vo. 1900. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., Colour a Sensation; Colours of Illuminated Bodies; Colours of Opaque and Transparent Bodies; Surface Colour.—II., Analysis of Light; Spectrum; Homogeneous Colours; Ready Method of Obtaining a Spectrum.—III., Examination of Solar Spectrum; The Spectroscope and Its Construction; Colourists' Use of the Spectroscope.—IV., Colour by Absorption; Solutions and Dyed Fabrics; Dichroic Coloured Fabrics in Gaslight.—V., Colour Primaries of the Scientist *versus* the Dyer and Artist; Colour Mixing by Rotation and Lye Dyeing; Hue, Purity, Brightness; Tints; Shades, Scales, Tones, Sad and Sombre Colours.—VI., Colour Mixing: Pure and Impure Greens, Orange and Violets; Large Variety of Shades from few Colours; Consideration of the Practical Primaries: Red, Yellow and Blue.—VII., Secondary Colours; Nomenclature of Violet and Purple Group; Tints and Shades of Violet; Changes in Artificial Light.—VIII., Tertiary Shades; Broken Hues; Absorption Spectra of Tertiary Shades.—Appendix: Four Plates with Dyed Specimens Illustrating Text.—Index.

Press Opinions.

"The work has evidently been prepared with great care."—*Halifax Courier.*

"The volume, which is clearly and popularly written, should prove of the utmost service to all who are concerned with the practical use of colours, whether as dyers or painters."—*Scotsman.*

"We have no hesitation in advising the purchase of the present volume by dyers and calico printers, as containing a mass of most useful information at a nominal price."—*Irish Textile Journal.*

"Mr. Paterson's work . . . will be found exceedingly helpful, not only to the practical colourist, but also to students in our textile colleges, by forming a useful complement to their class lectures."—*Wakefield Express.*

". . . The author is a dyer, and in his concluding chapters keeps well before him the special wants and requirements of dyers. He writes pleasantly and lucidly, and there is no difficulty in following him, although here and there a lapse into ambiguousness occurs."—*Textile Mercury.*

COLOUR MATCHING ON TEXTILES. A Manual intended for the use of Students of Colour Chemistry, Dyeing and Textile Printing. By DAVID PATERSON, F.C.S. Coloured Frontispiece. Twenty-nine Illustrations and Fourteen Specimens of Dyed Fabrics Illustrating Text. Demy 8vo. 132 pp. 1901. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., Colour Vision and Structure of the Eye—Perception of Colour—Primary and Complementary Colour Sensations.—II., Daylight for Colour Matching—Selection of a Good Pure Light—Diffused Daylight, Direct Sunlight, Blue Skylight, Variability of Daylight, etc., etc.—III., Matching of Hues—Purity and Luminosity of Colours—Matching Bright Hues—Aid of Tinted Films—Matching Difficulties Arising from Contrast.—IV., Examination of Colours by Reflected and Transmitted Lights—Effect of Lustre and Transparency of Fibres in Colour Matching.—V., Matching of Colours on Velvet Pile—Optical Properties of Dyestuffs, Dichroism, Fluorescence.—VI., Use of Tinted Mediums—Orange Film—Defects of the Eye—Yellowing of the Lens—Colour Blindness, etc.—VII., Matching of Dyed Silk Trimmings and Linings and Bindings—Its Difficulties—Behaviour of Shades in Artificial Light—Colour Matching of Old Fabrics, etc.—VIII., Examination of Dyed Colours under the Artificial Lights—Electric Arc, Magnesium and Dufton, Gardner Lights, Welsbach, Acetylene, etc.—Testing Qualities of an Illuminant.—IX., Influence of the Absorption Spectrum in Changes of Hue under the Artificial Lights—Study of the Causes of Abnormal Modifications of Hue, etc.

Press Opinions.

"It should form a part of the library of every dyer and colourist in the United Kingdom and indeed of every English-speaking country."—*Dyer and Calico Printer.*

"We recommend it to every one who has anything to do with colour matching, even to merchants dealing in colouring goods."—*Indian Textile Journal.*

Reissue of

THE ART OF DYEING WOOL, SILK AND COTTON. Translated from the French of M. HELLOT, M. MACQUER and M. LE PILEUR D'APLIGNY. First Published in English in 1789. Six Plates. Demy 8vo. 446 pp. 1901. Price 5s.; India and Colonies, 5s. 6d.; Other Countries, 6s.; strictly net.

Contents.

Part I., **The Art of Dyeing Wool and Woollen Cloth, Stuffs, Yarn, Worsted, etc.**
Part II., **The Art of Dyeing Silk.**
Part III., **The Art of Dyeing Cotton and Linen Thread, together with the Method of Stamping Silks, Cottons, etc.**

Press Opinions.

"The book has been produced in excellent style and should be of great assistance to dyers."—*Drapers' Record.*

"Its reissue cannot fail to be of deep interest to all engaged in textile manufacture."—*Macclesfield Courier.*

THE DYEING OF COTTON FABRICS: A Practical Handbook for the Dyer and Student. By FRANKLIN BEECH, Practical Colourist and Chemist. 272 pp. Forty-four Illustrations of Bleaching and Dyeing Machinery. Demy 8vo. 1901. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., Structure and Chemistry of the Cotton Fibre.—II., Scouring and Bleaching of Cotton.—III., Dyeing Machinery and Dyeing Manipulations.—IV., Principals and Practice of Cotton Dyeing—1, Direct Dyeing; 2, Direct Dyeing followed by Fixation with Metallic Salts; 3, Direct Dyeing followed by Fixation with Developers; 4, Direct Dyeing followed by Fixation with Couplers; 5, Dyeing on Tannic Mordant; 6, Dyeing on Metallic Mordant; 7, Production of Colour Direct upon Cotton Fibres; 8, Dyeing Cotton by Impregnation with Dye-stuff Solution.—V., Dyeing Union (Mixed Cotton and Wool) Fabrics.—VI., Dyeing Half Silk (Cotton-Silk, Satin) Fabrics.—VII., Operations following Dyeing—Washing, Soaping, Drying.—VIII., Testing of the Colour of Dyed Fabrics.—IX., Experimental Dyeing and Comparative Dye Testing.—Index.

The book contains numerous recipes for the production on Cotton Fabrics of all kinds of a great range of colours, thus making it of great service in the Dyehouse, while to the Student it is of value in that the scientific principles which underlie the operations of dyeing are clearly laid down.

THE DYEING OF WOOLLEN FABRICS. By FRANKLIN BEECH, Practical Colourist and Chemist. Thirty-three Illustrations. Demy 8vo. 228 pp. 1902. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d. net.

Contents.

Chapters I., The Wool Fibre—Structure, Composition and Properties.—II., Processes Preparatory to Dyeing—Scouring and Bleaching of Wool.—III., Dyeing Machinery and Dyeing Manipulations—Loose Wool Dyeing, Yarn Dyeing and Piece Dyeing Machinery.—IV., The Principles and Practice of Wool Dyeing—Properties of Wool Dyeing—Methods of Wool Dyeing—Groups of Dyes—Dyeing with the Direct Dyes—Dyeing with Basic Dyes—Dyeing with Acid Dyes—Dyeing with Mordant Dyes—Level Dyeing—Blacks on Wool—Reds on Wool—Mordanting of Wool—Orange Shades on Wool—Yellow Shades on Wool—Green Shades on Wool—Blue Shades on Wool—Violet Shades on Wool—Brown Shades on Wool—Mode Colours on Wool—V., Dyeing Union (Mixed Cotton Wool) Fabrics.—VI., Dyeing of Gloria.—VII., Operations following Dyeing—Washing, Soaping, Drying.—VIII., Experimental Dyeing and Comparative Dye Testing.—IX., Testing of the Colour of Dyed Fabrics.—Index.

COTTON SPINNING (First Year). By THOMAS THORNLEY, Spinning Master, Bolton Technical School. 160 pp. Eighty-four Illustrations. Crown 8vo. 1901. Price 3s.; Abroad, 3s. 6d.; strictly net.

Contents.

Syllabus and Examination Papers of the City and Guilds of London Institute.—Chapters I., Cultivation, Classification, Ginning, Baling and Mixing of the Raw Cotton.—II., Bale-Breakers, Mixing Lattices and Hopper Feeders.—III., Opening and Scutching.—IV., Carding.—Index to Illustrations.—General Index.

COTTON SPINNING (Intermediate, or Second Year). By THOMAS THORNLEY. 180 pp. Seventy Illustrations. Crown 8vo. 1901. Price 5s.; India and British Colonies, 5s. 6d.; Other Countries, 6s.; strictly net.

Contents.

Syllabuses and Examination Papers of the City and Guilds of London Institute.—Chapters I., The Combing Process.—II., The Drawing Frame.—III., Bobbin and Fly Frames.—IV., Mule Spinning.—V., Ring Spinning.—Index to Illustrations.—General Index.

COTTON SPINNING (Honours, or Third Year). By THOMAS THORNLEY. 216 pp. Seventy-four Illustrations. Crown 8vo. 1901. Price 5s.; India and British Colonies, 5s. 6d.; Other Countries, 6s.; strictly net.

Contents.

Syllabuses and Examination Papers of the City and Guilds of London Institute.—Chapters I., Cotton.—II., The Practical Manipulation of Cotton Spinning Machinery.—III., Doubling and Winding.—IV., Reeling.—V., Warping.—VI., Production and Costs.—VII., Main Driving.—VIII., Arrangement of Machinery and Mill Planning.—IX., Waste and Waste Spinning.—Index to Illustrations.—General Index.

Opinions of Spinning Teachers.

"The work (Vol. I.) contains a large amount of valuable information."—Mr. Jas. Tasher, Preston.

"They are certainly the best published on the subject."—Mr. John Kerfoot, Leigh.

"Admirably fulfils the object in view, *viz.*, a concise guide to the students preparing for the City and Guilds Examination Course."—Mr. Jas. W. Lomax, Bolton.

"I have carefully read the book, and do not hesitate in saying that I consider it will undoubtedly be a boon to cotton spinning students for three, among other, reasons: (1) The store of information on different makers' machines; (2) it shows the student how he should consider the questions proposed at the examinations; and (3) the methods he should adopt in answering same."—Samuel Ward, Teacher in Cotton Spinning, Glossop and Openshaw.

COTTON COMBING MACHINES. By THOS. THORNLEY, Spinning Master, Technical School, Bolton. Demy 8vo. 117 Illustrations. 300 pp. 1902. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d. net.

Contents.

Chapters I., The Sliver Lap Machine and the Ribbon Cap Machine.—II., General Description of the Heilmann Comber.—III., The Cam Shaft.—IV., On the Detaching and Attaching Mechanism of the Comber.—V., Resetting of Combers.—VI., The Erection of a Heilmann Comber.—VII., Stop Motions: Various Calculations—VIII., Various Notes and Discussions.—IX., Cotton Combing Machines of Continental Make.—Index.

Books for Mining Engineers and Steam Users.

RECOVERY WORK AFTER PIT FIRES. A Description of the Principal Methods Pursued, especially in Fiery Mines, and of the Various Appliances Employed, such as Respiratory and Rescue Apparatus, Dams, etc. By ROBERT LAMPRECHT, Mining Engineer and Manager. Translated from the German. Illustrated by Six large Plates, containing Seventy-six Illustrations. 175 pp., demy 8vo. 1901. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net.

Contents.

Preface.—I., **Causes of Pit Fires:** 1, Fires Resulting from the Spontaneous Ignition of Coal; 2, Fires Caused by Burning Timber; 3, Fires Caused by Fire-damp Explosions.—II., **Preventive Regulations:** 1, The Outbreak and Rapid Extension of a Shaft Fire can be most reliably prevented by Employing little or no Combustible Material in the Construction of the Shaft; 2, Precautions for Rapidly Localising an Outbreak of Fire in the Shaft; 3, Precautions to be Adopted in case those under 1 and 2 Fail or Prove Inefficient Precautions against Spontaneous Ignition of Coal. Precautions for Preventing Explosions of Fire-damp and Coal Dust. Employment of Electricity in Mining, particularly in Fiery Pits. Experiments on the Ignition of Fire-damp Mixtures and Clouds of Coal Dust by Electricity.—III., **Indications of an Existing or Incipient Fire.**—IV., **Appliances for Working in Irrespirable Gases:** 1, Respiratory Apparatus; 2, Apparatus with Air Supply Pipes, (*a*) The Bremen Smoke Helmet, (*b*) The Müller Smoke Helmet, (*c*) The Stolz Rescue Mask; 3, Reservoir Apparatus; 4, Oxygen Apparatus. The Schwann Respiratory Apparatus. The Fleuss Respiratory Apparatus. The Improved Walcher-Gärtner Pneumatophor, (*a*) The Single Bottle Apparatus, Instructions for Using the Pneumatophor, Taking to Pieces and Resetting the Apparatus ready for Use; (*b*) Two Bottle Apparatus (Shamrock Type). The Neupert Rescue Apparatus (The Mayer-Pilar System).—V. **Extinguishing Pit Fires:** (*a*) Chemical Means; (*b*) Extinction with Water. Dragging down the Burning Masses and Packing with Clay; (*c*) Insulating the Seat of the Fire by Dams. Dam Building. Dam Work in the Fiery Pits of Southern Hungary: (*a*) Cross-dams of Clay; (*b*) Masonry Dams, Gallery Linings. Wagner's Portable Safety Dam. Analyses of Fire Gases. Isolating the Seat of a Fire with Dams: Working in Irrespirable Gases ("Gas-diving"): 1, Air-Lock Work (Horizontal Advance) on the Mayer System as Pursued at Karwin in 1894; 2, Air-Lock Work (Horizontal Advance) by the Mauerhofer Modified System. Vertical Advance. Mayer System. Complete Isolation of the Pit. Flooding a

Burning Section isolated by means of Dams. Wooden Dams: (*a*) Upright Balk Dams; (*b*) Horizontal Balk Dams; (*c*) Wedge Dams, Masonry Dams. Examples of Cylindrical and Dome-shaped Dams. Dam Doors: Flooding the Whole Pit.—VI., **Rescue Stations:** (*a*) Stations above Ground; (*b*) Underground Rescue Stations.—VII., **Spontaneous Ignition of Coal in Bulk.**—Index.

Illustrations.

Sheet I., **Respiratory and Rescue Appliances—Precautions against Fire.** Sheet II., **Respiratory and Rescue Apparatus.** Sheet III., **Respiratory and Rescue Apparatus—Stretchers.** Sheet IV., **Dams.** Sheet V., **Signalling Appliances—Dam Construction—Cable Laying.** Sheet VI., **Working with Diving Gear in Irrespirable Gases—Gallery Work.** Sheet VII., **Working with Diving Gear in Irrespirable Gases (Mayer System)—Appliances in the Shaft.**

Press Opinions.

"A work of this extremely valuable character deserves to be made widely known amongst colliery managers and mining engineers at home and abroad."—*Coal and Iron.*

"This book is, in a manner, unique. The literature of mining accidents is fairly extensive, but it consists largely of departmental Blue Books."—*Sheffield Daily Telegraph.*

"A concise and lucid description of the principal methods pursued, especially in fiery mines, and of the various appliances employed, such as respiratory and rescue apparatus, dams, etc."—*Staffs Advertiser.*

"The prevention of spontaneous combustion in collieries and the extinction of underground fires are duties that fall heavily on many colliery managers. They should, therefore, welcome this translation of Mr. Lamprecht's German treatise."—*Ironmonger.*

THE PREVENTION OF SMOKE. Combined with the Economical Combustion of Fuel. By W. C. POPPLEWELL, M.Sc., A.M.Inst., C.E., Consulting Engineer. Forty-six Illustrations. 190 pp. 1901. Demy 8vo. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Introductory.—Chapters I., Fuel and Combustion.—II., Hand Firing in Boiler Furnaces.—III., Stoking by Mechanical Means.—IV., Powdered Fuel.—V., Gaseous Fuel.—VI., Efficiency and Smoke Tests of Boilers.—VII., Some Standard Smoke Trials.—VIII., The Legal Aspect of the Smoke Question.—IX., The Best Means to be adopted for the Prevention of Smoke.—Index.

Press Opinions.

"Everybody interested in smoke prevention will derive the greatest benefit from Mr. Popplewell's treatise, and will learn much that is new to them."—*Public Health Engineer.*

"The Manchester expert who writes this book is thoroughly equipped for the task, and he has produced a work which ought to be in the hands of all Sanitary Inspectors and Health Committees, and it would be a useful present from manufacturers to stokers, instead of possibly spending the value of the volume in payment of fines."—*Sheffield Independent.*

GAS AND COAL DUST FIRING. A Critical Review of the Various Appliances Patented in Germany for this purpose since 1885. By ALBERT PÜTSCH. 130 pp. Demy 8vo. 1901. Translated from the German. With 103 Illustrations. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Generators—Generators Employing Steam—Stirring and Feed Regulating Appliances—Direct Generators—Burners—Regenerators and Recuperators—Glass Smelting Furnaces—Metallurgical Furnaces—Pottery Furnace—Coal Dust Firing.—Index.

Press Opinions.

"The work is worthy of perusal by all consumers of fuel. It is exceedingly well printed and illustrated."—*Chemical Trade Journal.*

"The book will appeal with force to the manufacturer as well as to the technical student, whilst it is also of far more than average interest to the general reader."—*Halifax Guardian.*

"The importance that gas and coal dust firing have attained of recent years, and especially the great interest attaching of late to the question of coal dust firing, makes the appearance of the present volume most opportune."—*Iron and Coal Trades Review.*

Books on Plumbing, Decorating, Metal Work, etc., etc.

EXTERNAL PLUMBING WORK. A Treatise on Lead Work for Roofs. By JOHN W. HART, R.P.C. 180 Illustrations. 270 pp. Demy 8vo. Second Edition Revised. 1902. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d. strictly net.

Contents.

Chapters I., Cast Sheet Lead.—II., Milled Sheet Lead.—III., Roof Cesspools.—IV., Socket ...es.—V., Drips.—VI., Gutters.—VII., Gutters (continued).—VIII., Breaks.—IX., Circular ...eaks.—X., Flats.—XI., Flats (continued).—XII., Rolls on Flats.—XIII., Roll Ends.—XIV., ...ll Intersections.—XV., Seam Rolls.—XVI., Seam Rolls (continued).—XVII., Tack Fixings. XVIII., Step Flashings.—XIX., Step Flashings (continued).—XX., Secret Gutters.—XXI., ...akers.—XXII., Hip and Valley Soakers.—XXIII., Dormer Windows.—XXIV., Dormer ...indows (continued).—XXV., Dormer Tops.—XXVI., Internal Dormers.—XXVII., Skylights. XXVIII., Hips and Ridging.—XXIX., Hips and Ridging (continued).—XXX., Fixings for ...ips and Ridging.—XXXI., Ornamental Ridging.—XXXII., Ornamental Curb Rolls.—XXXIII., ...urb Rolls.—XXXIV., Cornices.—XXXV., Towers and Finials.—XXXVI., Towers and Finials ...ontinued).—XXXVII.,Towers and Finials (continued).—XXXVIII., Domes.—XXXIX., Domes ...ontinued).—XL., Ornamental Lead Work.—XLI., Rain Water Heads.—XLII., Rain Water ...eads (continued).—XLIII., Rain Water Heads (continued).

Press Opinions.

"This is an eminently practical and well-illustrated volume on the management of external ...ad work."—*Birmingham Daily Post.*

"It is thoroughly practical, containing many valuable hints, and cannot fail to be of great ...enefit to those who have not had large experience."—*Sanitary Journal.*

"Works on sanitary plumbing are by no means rare, but treatises dealing with external ...lumbing work are sufficiently scarce to ensure for Mr. Hart's new publication a hearty recep...ion."—*The Ironmonger.*

HINTS TO PLUMBERS ON JOINT WIPING, PIPE BENDING AND LEAD BURNING.

Third Edition, Revised and Corrected. By JOHN W. HART, R.P.C. 184 Illustrations. 313 pp. Demy 8vo. 1901. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Introduction.—C apters I., Pipe Bending.—II., Pipe Bending (continued).—III., Pipe Bending (continued).—IV., Square Pipe Bendings.—V., Half-circular Elbows.—VI., Curved Bends on Square Pipe.—VII., Bossed Bends.—VIII., Curved Plinth Bends.—IX., Rain-water Shoes on Square Pipe.—X., Curved and Angle Bends.—XI., Square Pipe Fixings.—XII., Joint-wiping.—XIII., Substitutes for Wiped Joints.—XIV., Preparing Wiped Joints.—XV., Joint Fixings.—XVI., Plumbing Irons.—XVII., Joint Fixings.—XVIII., Use of "Touch" in Solder...ng.—XIX., Underhand Joints.—XX., Blown and Copper Bit Joints.—XXI., Branch Joints.—XXII., Branch Joints (continued).—XXIII., Block Joints.—XXIV., Block Joints (continued).—XXV., Block Fixings.—XXVI., Astragal Joints—Pipe Fixings.—XXVII., Large Branch Joints.—XXVIII., Large Underhand Joints.—XXIX., Solders.—XXX., Autogenous Soldering or Lead Burning.—Index.

Press Opinions.

"Rich in useful diagrams as well as in hints."—*Liverpool Mercury.*

"The papers are eminently practical, and go much farther into the mysteries they describe than the title 'Hints' properly suggests."—*Scotsman.*

"The articles are apparently written by a thoroughly practical man. As a practical guide the book will doubtless be of much service."—*Glasgow Herald.*

"So far as the practical hints in this work are concerned, it will be useful to apprentices and students in technical schools, as it deals mainly with the most important or difficult branches of the plumber's craft, *viz.*, joint wiping, pipe bending and lead burning. . . . 'Hints' are the most useful things to an apprentice, and there are many in this work which are not to be found in some of the text-books."—*English Mechanic.*

"22 PRYME STREET, HULL, *24th November*, 1894.

"Gentlemen,—Your books to hand for which accept my best thanks, also for circulars. I myself got one of J. W. Hart's books on Plumbing from your traveller, and having looked through the same I can safely recommend it as being the best book I have seen. Mr. J. W. Hart treats exhaustively upon soldering and pipe bending, which are two of the most essential branches in the plumbing trade."

THE PRINCIPLES AND PRACTICE OF DIPPING, BURNISHING, LACQUERING AND BRONZING BRASS WARE.

By W. NORMAN BROWN. 35 pp. Crown 8vo. 1900. Price 2s.; Abroad, 2s. 6d.; strictly net.

Contents.

Chapters I., Cleansing and Dipping; Boiling up and Cleansing; Dipping.—II., Scratch-brushing and Burnishing; Polishing; Burnishing.—III., Lacquering; Tools; Lacquers.—IV., Bronzing; Black Bronzing; Florentine Red Bronzing; Green Bronzing.—Index.

Press Opinions.

"Mr. Brown is clearly a master of his craft, and has also the immense advantage of being able to convey his instructions in a manner at once clear and concise."—*Leicester Post.*

"A thoroughly practical little treatise on the subject in all its branches, and one which should be in the hands of every tradesman or amateur who has lacquering to do."—

WORKSHOP WRINKLES for Decorators, Painters, Paperhangers and Others. By W. N. BROWN. Crown 8vo. 128 pp. 1901. Price 2s. 6d.; Abroad, 3s.; strictly net.

Contents.

Parts I., Decorating.—II., Painting.—III., Paper-hanging.—IV., Miscellaneous. Arranged in alphabetical order.

Press Opinion.

"Decorators, painters and amateurs will find this a comprehensive work of reference on nearly every subject they are in need of." —*Building News.*

HOUSE DECORATING AND PAINTING. By W. NORMAN BROWN. Eighty-eight Illustrations. 150 pp. Crown 8vo. 1900. Price 3s. 6d.; India and Colonies, 4s.; Other Countries, 4s. 6d. strictly net.

Contents.

Chapters I., Tools and Appliances.—II., Colours and Their Harmony.—III., Pigments and Media.—IV., Pigments and Media.—V., Pigments and Media.—VI., Pigments and Media.—VII., Preparation of Work, etc.—VIII., Application of Ordinary Colour.—IX., Graining.—X., Graining.—XI., Graining.—XII., Gilding.—XIII., Writing and Lettering.—XIV., Sign Painting.—XV., Internal Decoration.—Index.

Press Opinion.

"The author is evidently very thoroughly at home in regard to the technical subjects he has set himself to elucidate, from the mechanical rather than the artistic point of view, although the matter of correctness of taste is by no means ignored. Mr. Brown's style is directness itself, and there is no tyro in the painting trade, however mentally ungifted, who could fail to carry away a clearer grasp of the details of the subject after going over the performance."—*Building Industries.*

A HISTORY OF DECORATIVE ART. By W. NORMAN BROWN. Thirty-nine Illustrations. 96 pp. Crown 8vo. 1900. Price 2s. 6d.; Abroad, 3s.; strictly net.

Contents.

Chapters I., Primitive and Prehistoric Art.—II., Egyptian Art.—III., Assyrian Art.—IV., The Art of Asia Minor.—V., Etruscan Art.—VI., Greek Art.—VII., Roman Art.—VIII., Byzantine Art.—IX., Lombard or Romanesque Art.—X., Gothic Art.—XI., Renaissance Art.—XII., The Victorian Period.—Index.

Press Opinion.

"In the course of a hundred pages with some forty illustrations Mr. Brown gives a very interesting and comprehensive survey of the progress and development of decorative art. It cannot, of course, be pretended that in the limited space named the subject is treated exhaustively and in full detail, but it is sufficiently complete to satisfy any ordinary reader; indeed, for general purposes, it is, perhaps, more acceptable than a more elaborate treatise."—*Midland Counties Herald.*

A HANDBOOK ON JAPANNING AND ENAMELLING FOR CYCLES, BEDSTEADS, TINWARE, ETC. By WILLIAM NORMAN BROWN. 52 pp. and Illustrations. Crown 8vo. 1901. Price 2s.; Abroad, 2s. 6d.; net.

Contents.

A Few Words on Enamelling—Appliances and Apparatus—Japans or Enamels—To Test Enamel for Lead—Japanning or Enamelling Metals—Japanning Tin, such as Tea Trays, and similar Goods—Enamelling Old Work—Enamel for Cast Iron—Enamel for Copper Cooking Utensils—The Enamelling Stove—Enamelling Bedsteads, Frames and similar large pieces—Paints and Varnishes for Metallic Surfaces—Varnishes for Ironwork—Blacking for Iron—Processes for Tin Plating—Galvanising—Metal Polishes—Colours for Polished Brass—A Golden Varnish for Metal—Painting on Zinc—Carriage Varnish—Japanese Varnish and its Application.—Index

THE PRINCIPLES OF HOT WATER SUPPLY. By JOHN W. HART, R.P.C. With 129 Illustrations. 1900. 177 pp., demy 8vo. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., Water Circulation.—II., The Tank System.—III., Pipes and Joints.—IV., The Cylinder System.—V., Boilers for the Cylinder System.—VI., The Cylinder System.—VII., The Combined Tank and Cylinder System.—VIII., Combined Independent and Kitchen Boiler.—IX., Combined Cylinder and Tank System with Duplicate Boilers.—X., Indirect Heating and Boiler Explosions.—XI., Pipe Boilers.—XII., Safety Valves.—XIII., Safety Valves.—XIV., The American System.—XV., Heating Water by Steam.—XVI., Steam Kettles and Jets.—XVII., Heating Power of Steam.—XVIII., Covering for Hot Water Pipes.—Index.

Brewing and Botanical.

HOPS IN THEIR BOTANICAL, AGRICULTURAL AND TECHNICAL ASPECT, AND AS AN ARTICLE OF COMMERCE. By EMMANUEL GROSS, Professor at the Higher Agricultural College, Tetschen-Liebwerd. Translated from the German. Seventy-eight Illustrations. 1900. 340 pp. Demy 8vo. Price 12s. 6d.; India and Colonies, 13s. 6d.; Other Countries, 15s.; strictly net.

Contents.

PART I., HISTORY OF THE HOP.

PART II., THE HOP PLANT. Introductory.—The Roots.—The Stem and Leaves.—Inflorescence and Flower: Inflorescence and Flower of the Male Hop; Inflorescence and Flower of the Female Hop.—The Fruit and its Glandular Structure: The Fruit and Seed.—Propagation and Selection of the Hop.—Varieties of the Hop: (*a*) Red Hops; (*b*) Green Hops; (*c*) Pale Green Hops.—Classification according to the Period of Ripening: 1. Early August Hops; 2. Medium Early Hops; 3. Late Hops.—Injuries to Growth: Malformations; Diseases Produced by Conditions of Soil and Climate: 1. Leaves Turning Yellow, 2. Summer or Sunbrand, 3. Cones Dropping Off, 4. Honey Dew, 5. Damage from Wind, Hail and Rain; Vegetable Enemies of the Hop: Animal Enemies of the Hop.—Beneficial Insects on Hops.

PART III., CULTIVATION. The Requirements of the Hop in Respect of Climate, Soil and Situation: Climate; Soil; Situation.—Selection of Variety and Cuttings.—Planting a Hop Garden: Drainage; Preparing the Ground; Marking-out for Planting; Planting; Cultivation and Cropping of the Hop Garden in the First Year.—Work to be Performed Annually in the Hop Garden: Working the Ground; Cutting; The Non-cutting System; The Proper Performance of the Operation of Cutting: I. Method of Cutting: Close Cutting, Ordinary Cutting, The Long Cut, The Topping Cut; II. Proper Season for Cutting: Autumn Cutting, Spring Cutting; Manuring; Training the Hop Plant: Poled Gardens, Frame Training; Principal Types of Frames; Pruning, Cropping, Topping, and Leaf Stripping the Hop Plant; Picking, Drying and Bagging.—Principal and Subsidiary Utilisation of Hops and Hop Gardens.—Life of a Hop Garden; Subsequent Cropping.—Cost of Production, Yield and Selling Prices.

PART IV.—Preservation and Storage.—Physical and Chemical Structure of the Hop Cone.—Judging the Value of Hops.

PART V.—Statistics of Production.—The Hop Trade.—Index.

Press Opinions.

"The subject is dealt with fully in every little detail; consequently, even the veriest tyro can take away some useful information from its pages."—*Irish Farming World.*

"Like an oasis in the desert comes a volume upon the above subject."—*Hereford Times.*

"This is, in our opinion, the most scholarly and exhaustive treatise on the subject of hops that has been published."—*Brewers' Journal.*

Wood Waste Utilisation.

THE UTILISATION OF WOOD WASTE. Translated from the German of ERNST HUBBARD. Crown 8vo. 1902. Fifty Illustrations. Price 5s.; India and Colonies, 5s. 6d.; Other Countries, 6s. net.

Contents.

Chapters I., General Remarks on the Utilisation of Sawdust.—II., Employment of Sawdust as Fuel, with and without Simultaneous Recovery of Charcoal and the Products of Distillation.—III., Manufacture of Oxalic Acid from Sawdust—(1) Process with Soda Lye; (2) Thorn's Process; (3) Bohlig's Process.—IV., Manufacture of Spirit (Ethyl Alcohol) from Wood Waste—Patent Dyes (Organic Sulphides, Sulphur Dyes, or Mercapto Dyes).—V., Artificial Wood and Plastic Compositions from Sawdust—Production of Artificial Wood Compositions for Moulded Decorations.—VI., Employment of Sawdust for Blasting Powders and Gunpowders.—VII., Employment of Sawdust for Briquettes—Employment of Sawdust in the Ceramic Industry and as an Addition to Mortar—Manufasture of Paper Pulp from Wood—Casks.—VIII., Various Applications of Sawdust and Wood Refuse—Calcium Carbide—Manure—Wood Mosaic Plaques—Bottle Stoppers—Parquetry—Fire-lighters—Carborundum.—IX., The Production of Wood Wool—Bark.—Index

Foods and Sweetmeats.

THE MANUFACTURE OF PRESERVED FOODS AND SWEETMEATS: A Handbook of all the Processes for the Preservation of Flesh, Fruit and Vegetables, and for the Preparation of Dried Fruit, Dried Vegetables, Marmalades, Fruit-Syrups and Fermented Beverages, and of all kinds of Candies, Candied Fruit, Sweetmeats, Rocks, Drops, Dragées, Pralines, etc. By A. HAUSNER. With Twenty-eight Illustrations. Translated from the German of the third enlarged Edition. Crown 8vo. 225 pp. 1902. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d. net.

Contents.

Part I., **The Manufacture of Conserves.**—Chapters I., Introduction.—II., The Causes of the Putrefaction of Food.—III., The Chemical Composition of Foods.—IV., The Products of Decomposition.—V., The Causes of Fermentation and Putrefaction.—VI., Preservative Bodies.—VII., The Various Methods of Preserving Food.—VIII., The Preservation of Animal Food.—IX., Preserving Meat by Means of Ice.—X., The Preservation of Meat by Charcoal.—XI., Preservation of Meat by Drying.—XII., The Preservation of Meat by the Exclusion of Air.—XIII., The Appert Method.—XIV., Preserving Flesh by Smoking.—XV., Quick Smoking.—XVI., Preserving Meat with Salt.—XVII., Quick Salting by Air Pressure.—XVIII., Quick Salting by Liquid Pressure.—XIX., Gamgee's Method of Preserving Meat.—XX., The Preservation of Eggs.—XXI., Preservation of White and Yolk of Egg.—XXII., Milk Preservation.—XXIII., Condensed Milk.—XXIV., The Preservation of Fat.—XXV., Manufacture of Soup Tablets.—XXVI.—Meat Biscuits.—XXVII., Extract of Beef.—XXVIII., The Preservation of Vegetable Foods in General.—XXIX.—Compressing Vegetables.—XXX., Preservation of Vegetables by Appert's Method.—XXXI., The Preservation of Fruit.—XXXII., Preservation of Fruit by Storage.—XXXIII., The Preservation of Fruit by Drying.—XXXIV., Drying Fruit by Artificial Heat.—XXXV., Roasting Fruit.—XXXVI., The Preservation of Fruit with Sugar.—XXXVII., Boiled Preserved Fruit.—XXXVIII., The Preservation of Fruit in Spirit, Acetic Acid or Glycerine.—XXXIX., Preservation of Fruit without Boiling.—XL., Jam Manufacture.—XLI., The Manufacture of Fruit Jellies.—XLII., The Making of Gelatine Jellies.—XLIII., The Manufacture of "Sulzen."—XLIV., The Preservation of Fermented Beverages.

Part II., **The Manufacture of Candies.**—Chapters XLV., Introduction.—XLVI., The Manufacture of Candied Fruit.—XLVII., The Manufacture of Boiled Sugar and Caramel.—XLVIII., The Candying of Fruit.—XLIX., Caramelised Fruit.—L., The Manufacture of Sugar-Sticks, or Barley Sugar.—LI., Bonbon Making.—LII., Fruit Drops.—LIII., The Manufacture of Dragées.—LIV., The Machinery and Appliances used in Candy Manufacture.—LV., Dyeing Candies and Bonbons.—LVI., Essential Oils used in Candy Making.—LVII., Fruit Essences.—LVIII., The Manufacture of Filled Bonbons, Liqueur Bonbons and Stamped Lozenges.—LIX., Recipes for Jams and Jellies.—LX., Recipes for Bonbon Making.—LXI., Dragées.—Appendix.—Index.

Timber Trades.

TIMBER: A Comprehensive Study of Wood in all its Aspects (Commercial and Botanical), showing the Different Applications and Uses of Timber in Various Trades, etc. Translated from the French of PAUL CHARPENTIER, Expert Chemical Engineer, Assayer of the French Mint, etc., by JOSEPH KENNELL. Royal 8vo. 437 pp. 178 Illustrations. 1902. Price 12s. 6d.; India and Colonies, 13s. 6d.; Other Countries, 15s. net.

Contents.

Preface.—Part I., **Physical and Chemical Properties of Timber.**—Chapters I., Composition of the Vegetable Bodies—Chief Elements—M. Fremy's Researches.—II., Elementary Organs of Plants and especially of Forests.—III., Different Parts of Wood Anatomically and Chemically Considered.—IV., General Properties of Wood.

Part II., **Description of the Different Kinds of Wood.**—Chapters V., Principal Essences with Caducous Leaves.—VI., Coniferous Resinous Trees.

Part III., **Division of the Useful Varieties of Timber in the Different Countries of the Globe.**—Chapters VII., European Timber.—VIII., African Timber.—IX., Asiatic Timber—X., American Timber.—XI., Timber of Oceania.

Part IV., **Forests.**—Chapters XII., General Notes as to Forests; their Influence.—XIII. Opinions as to Sylviculture—Improvement of Forests.—XIV., Unwooding and Rewooding—Preservation of Forests.—XV., Exploitation of Forests.—XVI., Damage caused to Forests—Different Alterations.

Part V., **The Preservation of Timber.**—Chapters XVII., Generalities—Causes and Progress of Deterioration—History of Different Proposed Processes.—XVIII., Dessication—Superficial Carbonisation of Timber.—XIX., Processes by Immersion—Generalities as to

Antiseptics Employed.—XX., Injection Processes in Closed Vessels.—XXI., The Boucherie System, Based upon the Displacement of the Sap.—XXII., Processes for Making Timber Uninflammable.

Part VI., **Applications of Timber.**—Chapters XXIII., Generalities—Working Timber—Paving—Timber for Mines—Railway Traverses.—XXIV., Accessory Products—Gums—Works of M. Fremy—Resins—Barks—Tan—Application of Cork.—XXV., The Application of Wood to Art and Dyeing.—XXVI., Different Applications of Wood—Hard Wood—Distillation of Wood—Pyroligneous Acid—Oil of Wood—Distillation of Resins.—Index.

[*See also* "*Wood Waste Utilisation*," *p.* 33.]

Fancy Goods Manufacture.

THE ART OF DYEING AND STAINING MARBLE, ARTIFICIAL STONE, BONE, HORN, IVORY AND WOOD, AND OF IMITATING ALL SORTS OF WOOD.

A Practical Handbook for the Use of Joiners, Turners, Manufacturers of Fancy Goods, Stick and Umbrella Makers, Comb Makers, etc. Translated from the German of D. H. SOXHLET, Technical Chemist. Crown 8vo. 168 pp. 1902. Price 5s.; India and Colonies, 5s. 6d.; Other Countries, 6s. net.

Contents.

Preface.—Introduction.—Chapters I., Mordants and Stains: Acids, Alkalies, Iron Salts, Copper Salts, Aluminium Salts, Chromium Salts, Tin Salts, Lead Salts, Manganese Salts, Silver and Gold Salts.—II., Natural Dyes: Redwood, Red Sandalwood, Madder, Orchil, Cudbear, Lac-Dye, Cochineal, Saffron, Annatto, Safflower, Fustic, Fustet, Quercitron, Flavin, Turmeric, Weld and its substitutes, Persian Berries, Barberry Root, Indigo, Logwood, Cutch, Galls, Sumach, Knoppern.—III., Artificial Pigments: White Lead, Naples Yellow, Red Lead, Smalts, Ultra-Marine, Cinnabar, Prussian Blue, Orpiment, Realgar, Chrome Green, Chrome Yellow, Chrome Red, Chrome Orange, Mosaic Gold, Green Mineral Colours, Red Ochres, Rouge, Cadmium Yellow.—IV., Coal Tar Dyes: Reds, Yellows and Oranges, Blues, Violets, Greens, Browns, Grey and Black—Aniline Dyes Soluble in Fat: Resinate Colours, Aniline Lakes.—V., Staining Marble and Artificial Stone: Red, Violet, Blue, Green, Yellow, Orange, Brown, Black, Execution of Parti-Coloured Designs.—VI., Dyeing, Bleaching and Imitation of Bone, Horn and Ivory—Bone Bleaching—Dyeing Bone: Black, Red, Yellow, Blue, Violet, Green, Grey and Brown—Horn, Bleaching and Whitening—Dyeing Black, Grey, Brown, Blue, Green, Violet and Red—Imitation of Tortoiseshell for Combs: Yellows, Dyeing Nuts.—Ivory: Dyeing Black, Red, Yellow, Blue, Violet, Green, Grey and Brown—Further Remarks on Ivory Dyeing.—VII., Wood Dyeing: Black, Grey, Brown, Violet, Blue, Red, Yellow, Green—Imitation of Mahogany: Dark Walnut, Oak, Birch-Bark, Elder-Marquetry, Walnut, Walnut-Marquetry, Mahogany, Spanish Mahogany, Palisander and Rose Wood, Tortoiseshell, Oak, Ebony, Pear Tree—Black Dyeing Processes with Penetrating Colours.—VIII., Varnishes and Polishes: English Furniture Polish, Vienna Furniture Polish, Amber Varnish, Copal Varnish, Composition for Preserving Furniture.—Index.

Building and Architecture.

THE PREVENTION OF DAMPNESS IN BUILDINGS;

with Remarks on the Causes, Nature and Effects of Saline, Efflorescences and Dry-rot, for Architects, Builders, Overseers, Plasterers, Painters and House Owners. By ADOLF WILHELM KEIM. Translated from the German of the second revised Edition by M. J. SALTER, F.I.C., F.C.S., Member of the German Chemical Society of Berlin. Eight Coloured Plates and Thirteen Illustrations. Crown 8vo. 115 pp. 1902. Price 5s.; India and Colonies, 5s. 6d.; Other Countries, 6s. net.

Contents.

Part I.—Chapters I., The Various Causes of Dampness and Decay of the Masonry of Buildings, and the Structural and Hygienic Evils of the Same.—II., Precautionary Measures during Building against Dampness and Efflorescence.—III., Methods of Remedying Dampness and Efflorescences in the Walls of Old Buildings.—IV., The Artificial Drying of New Houses, as well as Old Damp Dwellings, and the Theory of the Hardening of Mortar.—V., New, Certain and Permanently Efficient Methods for Drying Old Damp Walls and Dwellings.

Part II.—Chapters I., The Cause and Origin of Dry-rot: its Injurious Effect on Health, its Destructive Action on Buildings, and its Successful Repression.—II., Methods of Preventing Dry-rot to be Adopted During Construction.—III., Old Methods of Preventing Dry-rot.—IV., Recent and More Efficient Remedies for Dry-rot.—Index.

Iron.

SIDEROLOGY: THE SCIENCE OF IRON (The Constitution of Iron Alloys and Slags). Translated from German of HANNS FREIHERR V. ZÜPTNER. 350 pp. Demy 8vo. Eleven Plates and Ten Illustrations. 1902. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s. net.

Contents.

Book I., **The Theory of Solution.**—Chapters I., Solutions.—II., Molten Alloys—Varieties of Solutions.—III., Osmotic Pressure.—IV., Relation between Osmotic Pressure and other Properties of Solutions.—V., Osmotic Pressure and Molecular Weight of the Dissolved Substance.—VI., Solutions of Gases.—VII., Solid Solutions.—VIII., Solubility.—IX., Diffusion.—X., Electrical Conductivity—Constitution of Electrolytes and Metals.—XI., Thermal Expansion.

Book II., **Micrography.**—Chapters I., General.—II., Microstructure.—III., The Micrographic Constituents of Iron.—IV., Relation between Micrographical Composition, Carbon-Content, and Thermal Treatment of Iron Alloys.—V., The Microstructure of Slags.

Book III., **Chemical Composition of the Alloys of Iron.**—Chapters I., Introduction.—II., Constituents of Iron Alloys—Carbon.—III., Constituents of the Iron Alloys, Carbon—Opinions and Researches on Combined Carbon.—IV., Opinions and Researches on Combined Carbon (*Continuation*).—V., Opinions and Researches on Combined Carbon (*Conclusion*).—VI., Applying the Curves of Solution deduced from the Curves of Recalescence to the Determination of the Chemical Composition of the Carbon present in Iron Alloys.—VII., The Constituents of Iron—Iron.—VIII., The Constituents of Iron Alloys—Manganese.—IX., Remaining Constituents of Iron Alloys—A Silicon.—X., Gases.

Book IV., **The Chemical Composition of Slag.**—Chapters I., Introductory.—II., Silicate Slags.—III., Calculating the Composition of Silicate Slags.—IV., Phosphate Slags.—V., Oxide Slags.—Appendix.—Index.

WORKS IN PREPARATION.

TREATISE ON CLOTH FINISHING. By ROBERT BEAUMONT, of Yorkshire College, Leeds.

WEAVING MACHINERY. Three Vols. By HARRY NISBET.

COLOUR TERMS: THEIR PROPER USE AND MEANING. By DAVID PATERSON.

USE OF WATER IN THE INDUSTRIAL ARTS.

CHEMISTRY OF DYE STUFFS. Translated from German of Dr. GEORG VON GEORGIEVICS. [*In the press.*

SUGAR REFINERS' HANDBOOK.

ART OF BOOKBINDING.

DENTAL METALLURGY.

PRELIMINARY COTTON SPINNING AND WEAVING. By WALTER BAILEY.

VENTILATION OF MINES. By ROBERT WABNER. Royal 8vo. Thirty Plates. About 250 pp.

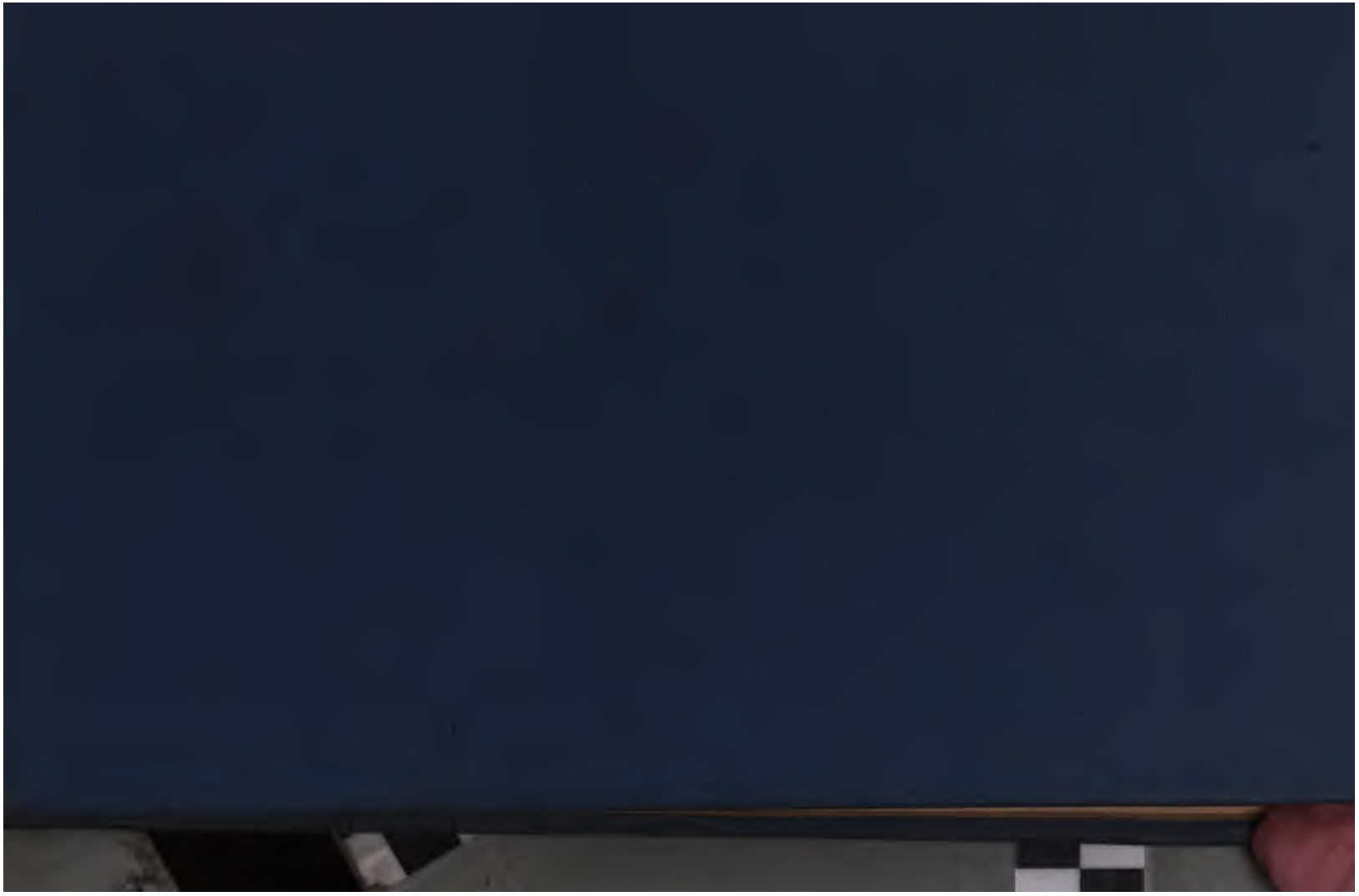
SIMPLE METHODS FOR TESTING PAINTERS' MATERIALS. By A. C. WRIGHT, M.A., B.Sc. Crown 8vo. Eight Illustrations. [*In the press.*

SEALING WAXES AND OTHER ADHESIVES. By H. C. STANDAGE.

HANDY GUIDES TO THE CHOICE OF BOOKS.

Vol. I. **PROSE FICTION.**

Vol. II. **CLASSIFIED GUIDE TO TECHNICAL, TRADE AND COMMERCIAL LITERATURE.**

Others to follow. [*In preparation.*

The Publishers will advise when any of the above books are ready to firms sending their addresses.